
Permeable Reactive Barriers for Inorganics

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FOREWORD

According to a recent market assessment study, the use of containment technologies as a remedial action will increase for contaminated sites. EPA's Technology Innovation Office (TIO) provided a grant through the National Network for Environmental Management Studies (NNEMS) to prepare a technology assessment report on subsurface barrier technologies that prevent the migration of contaminated material. This report was prepared by a graduate student from Duke University during the summer of 1999. It has been reproduced to help provide federal agencies, states, consulting engineering firms, private industries, and technology developers with information on the current status of this technology.

About the National Network for Environmental Management Studies (NNEMS)

NNEMS is a comprehensive fellowship program managed by the Environmental Education Division of EPA. The purpose of the NNEMS Program is to provide students with practical research opportunities and experiences.

Each participating headquarters or regional office develops and sponsors projects for student research. The projects are narrow in scope to allow the student to complete the research by working full-time during the summer or part-time during the school year. Research fellowships are available in Environmental Policy, Regulations, and Law; Environmental Management and Administration; Environmental Science; Public Relations and Communications; and Computer Programming and Development.

NNEMS fellows receive a stipend determined by the student's level of education and the duration of the research project. Fellowships are offered to undergraduate and graduate students. Students must meet certain eligibility criteria.

About this Report

This report is intended to provide a basic summary and current status of permeable reactive barriers for inorganics. It contains information gathered from a range of currently available sources, including project documents, reports, periodicals, Internet searches, and personal communication with involved parties. No attempts were made to independently confirm the resources used.

The report is available on the Internet at <http://www.clu-in.org>.

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Purpose

The scope of this document is to provide both general background information and specific details to remedial project managers on the treatment of inorganic contaminants with permeable reactive barriers (PRBs). Extensive literature exists on the use of PRBs (especially those made of zero valent iron) to remediate chlorinated solvent contamination. However, there are few sources that discuss both the general use of PRBs and the special considerations that must be taken into account when remediating groundwater contaminated with inorganic pollutants. The general background information presented includes explanations of how the technology works, advantages to using this technology over others, types of inorganic contaminants that can be treated, types of media that can be used, and troubleshooting. Also included are parameters to consider while using this technology, such as site characterization considerations, emplacement techniques, monitoring and maintenance concerns, and closure issues. The latter part of this document is more detailed and explains inorganic contaminant characteristics and behaviors that are important to consider when remediating groundwater. It also includes case studies of sites that have not been well documented, as of yet, in EPA publications and outlines of sites that have previously been discussed in other publications. The former are included to provide some new site information that may not be widely known, and the latter are included to provide readers who are not familiar with the history of PRBs some sense of the growing scope of their applications in inorganic contamination scenarios. (The Y-12 Oak Ridge, TN site has been well documented. However, a personal communication provided some important “lessons learned” that the author felt was valuable.)

1 General Background Information

1.1 Introduction

Between 1982 and 1997, pump and treat techniques were used solely to clean the contaminated groundwater at 89% of the Superfund sites being actively remediated (IBC, 1999). The pump and treat technology is energy intensive and cannot remove contaminants sorbed to the soil. Thus, researchers have developed a passive *in situ* method for treating contaminated plumes. This technology, termed “permeable reactive barriers/treatment zone” (PRB/PRTZ), is defined (USEPA, 1998) as:

An emplacement of reactive media in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and

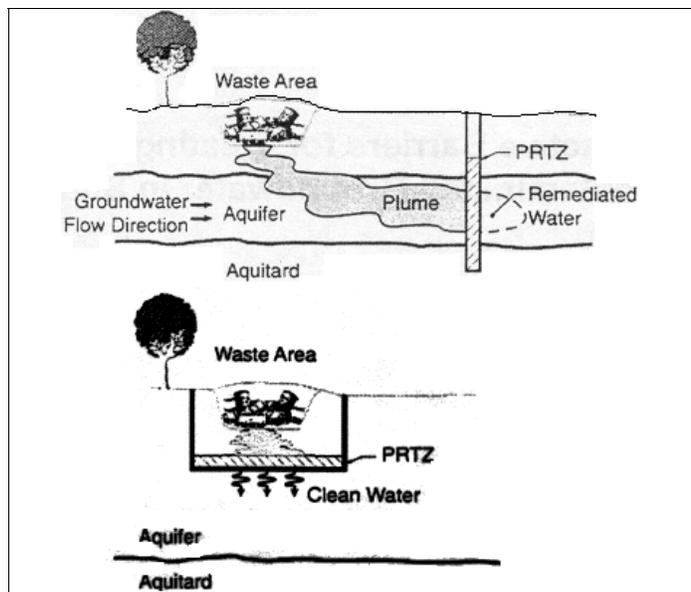


Figure 1. Illustration of Concept (USEPA, ITRC and RTDF, 1999).

transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down-gradient of the barrier.

The first full scale permeable reactive barrier was installed in Sunnyvale, Ca in 1994 to treat a plume of chlorinated solvents (IBC, 1999). The treatment of chlorinated aliphatic hydrocarbons by this technology has been successful and well documented. It was initially believed that chlorinated solvent degradation could only occur by biological means. However, these compounds can be degraded chemically by participating in reduction-oxidation (redox) reactions with the barrier materials, in which they act as oxidants and become reductively dechlorinated. The chlorine atoms are replaced by hydrogen atoms as the molecule is reduced to ethylene. The ethylene can ultimately be metabolized to carbon dioxide and water by aerobic micro-organisms.

Halogenated aliphatic compounds were found to be efficiently degraded with PRBs. Therefore, this technology's applications have been broadened to include the remediation of groundwater contaminated with inorganic contaminants, which is the focus of this discussion. Generally, these include metals, radionuclides, and nutrients.

It must be noted, however, that a fundamental difference exists between organic and inorganic contaminant remediation. Organic contaminants can be broken down into innocuous elements and compounds, such as carbon dioxide and water because they are molecules consisting of carbon, hydrogen, halogens, oxygen, and sometimes sulfur, phosphorous, and nitrogen, they. Conversely, most inorganic contaminants are themselves elements. They cannot be destroyed but can only change speciation. Therefore, remediation strategies must focus on transforming inorganics into forms that are nontoxic, not bioavailable, immobile, or capable of being removed from the subsurface.

These inorganic contaminants include, but are not limited to, chromium (Cr), nickel (Ni), lead (Pb), uranium (U), technetium (Tc), iron (Fe), manganese (Mn), selenium (Se), cobalt (Co), copper (Cu), cadmium (Cd), zinc (Zn), arsenic (As), nitrate (NO_3^- -N), sulfate (SO_4^{2-} -S), and phosphate (PO_4^{3-} -P) (USEPA, 1998). The characteristics that these elements have in common is that they can undergo redox reactions and can form solid precipitates with common groundwater constituents, such as carbonate (CO_3^{2-}), sulfide (S^{2-}), and hydroxide (OH^-). Some common sources of these contaminants are mine tailings, septic systems, and battery recycling/disposal facilities. Specific contaminants of interest are discussed in more detail in Section 3.1.

1.2 A Mechanistic Approach: How are Inorganic Contaminants Remediated?

Harmful groundwater constituents are available to biota and mobile if they are soluble in water. Several metals and nutrients exist as cations or oxyanions that are highly water soluble and highly toxic. PRBs act as barriers not to the groundwater, but to the compounds contaminating it (USEPA, 1998), by removing them by one of two methods: 1) introduction of a media that the contaminants will sorb to; or 2) introduction of a media that will alter the contaminant's behavior and decrease its bioavailability. This can be achieved either by changing its speciation or by providing a ligand for solid formation.

The latter option has been used more often, simply because sorption sites can quickly become saturated, leaving contaminants unreacted and reducing the barrier's permeability. A contaminant typically is altered to an innocuous form by changing its oxidation state. The oxidation state is the number of electrons in an atom's outer orbital and dictates the ways in which the atom will behave, i.e., what types of other atoms it can form interactions with and how it will partition in the subsurface (on solids, as gases, or dissolved in water). Therefore, only contaminants and barrier materials capable of existing at multiple oxidation states can participate in these types of transformations.

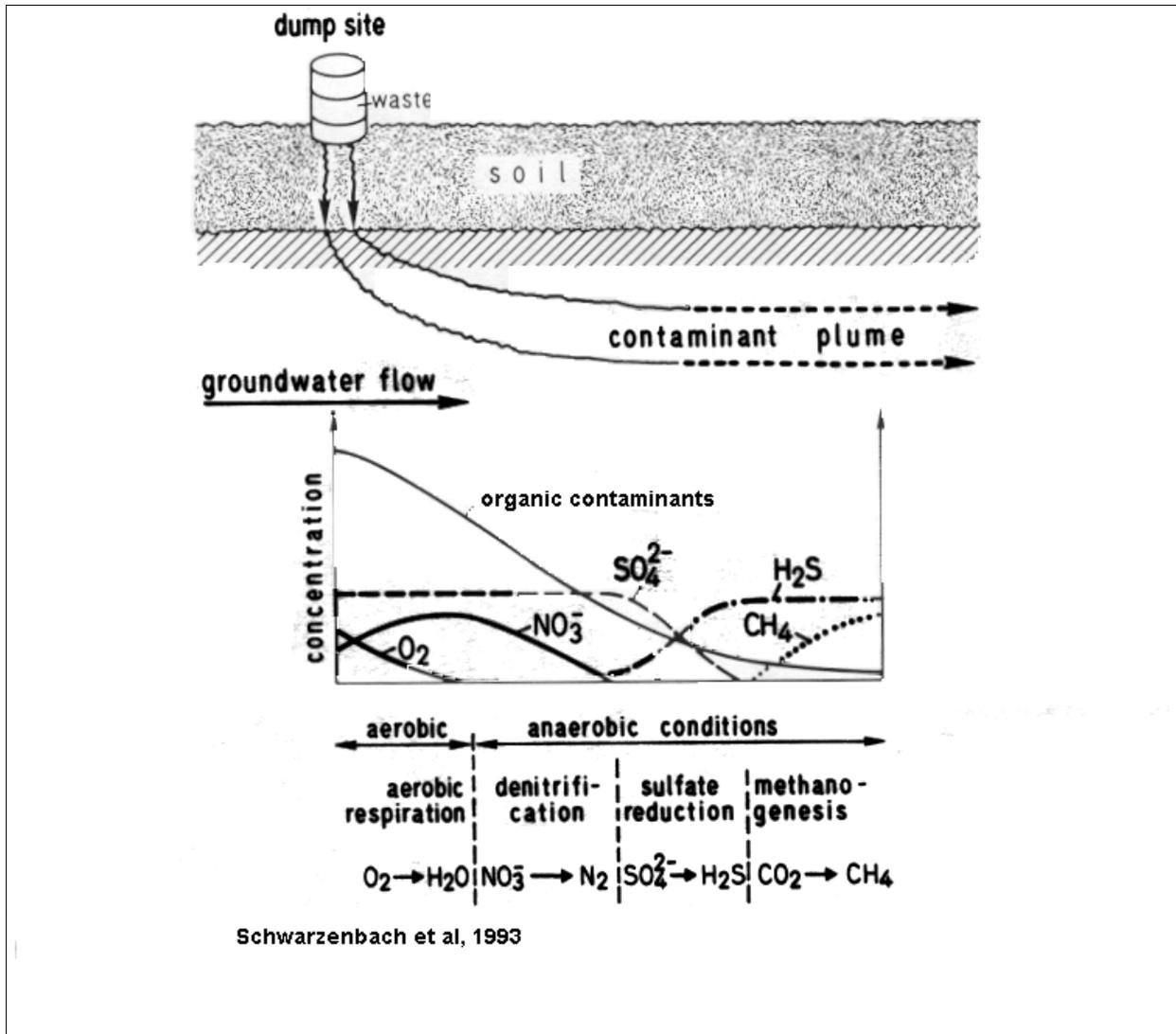


Figure 2. Changes in Redox Species along a Contaminant Plume.

A constituent's ability to participate in redox reactions can be quantified by its reduction potential (E_H). A high E_H indicates a strong ability to take electrons, i.e., to be reduced. Conversely, a low or negative E_H value is indicative of an electron donor. A great difference between E_H values for two species participating in a redox reaction results in the reaction being thermodynamically favorable. For example, O_2 serves as the terminal electron acceptor (TEA) for most biological reactions. Its reduction half-reaction has a very high E_H value. Therefore, a great

deal of energy can be obtained when it serves as the oxidant in a redox reaction (Sparks, 1995). Subsurface environments having gaseous or dissolved oxygen (i.e., oxic conditions) have a high E_H value. As an environment becomes anoxic, such as along many contaminant plumes, the E_H value decreases. The dominant electron acceptor for both biological and chemical reactions sequentially changes to weaker oxidants. Microbial activity and the types of reactions that contaminants can participate in coincide with these changes in redox conditions.

A contaminant can also become less mobile/toxic as an indirect result of a redox reaction. Metal sulfides are very insoluble. A solid's solubility constant (K_s) defines the product of the concentrations of the solid's constituents that can exist in the aqueous phase together. A complex with a low K_s value tends to precipitate, while one with a high K_s value tends to dissociate. Because metal sulfides typically have low K_s values, an input of S^{2-} into the system will not allow all of the metal ions to remain dissolved. They will form solid precipitates with the S^{2-} ions. For example, the K_s values for FeS, PbS, and ZnS are $10^{-17.3}$, $10^{-27.0}$, and $10^{-21.5}$, respectively (Snoeyink and Jenkins, 1980). To increase S^{2-} concentrations in the groundwater and encourage solid formation, barriers can be designed to promote the activity of sulfate reducing bacteria (SRB), micro-organisms that reduce SO_4^{2-} to S^{2-} .

Several metal contaminants can also form solid precipitates with CO_3^{2-} and OH^- . Therefore, barriers that contain these ions or encourage their formation can also be successful at removing soluble contaminant ions from the groundwater. A solid is typically not bioavailable or mobile. Therefore, it is the preferred form of a contaminant. These types of media will be further discussed in Section 1.4.2.

1.3 Treatment Media Types

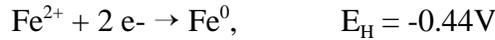
The types of contaminants present and the reactions needed to remove them from the aqueous phase dictate which types of media are desirable. Besides being capable of contaminant removal, the chosen medium should be low in cost, easy to obtain, devoid of hazardous materials so that groundwater is not secondarily contaminated, long lasting, made of uniform particle size to prevent plugging and to allow model predictions to be accurate, and made of large enough particles so that groundwater flow is not restricted (USEPA, 1998). Particle size also must be optimized because reactivity and kinetics are based upon the surface area available for interactions (Gavaskar *et al.*, 1998).

1.3.1 Barriers That Utilize Redox Reactions

1.3.1.1 Zero Valent Iron (ZVI)

The most extensively used medium is zero valent iron (ZVI), or Fe^0 . It is a byproduct of the auto parts manufacturing industry, and therefore is readily available. Residual oils and greases are burned off in a kiln, so that they are not present to interfere with reactivity. However, small amounts of residual carbon from the burning remain. Trace metals, such as magnesium, are also frequently left on the filings (USEPA, ITRC and RTDF, 1999).

Iron commonly exists in one of three oxidation states: 0, +2, and +3. It is thermodynamically favorable for Fe⁰ to become oxidized to Fe²⁺ by the following reaction:



(NATO, 1998).

By convention, a half reaction is always written as a reduction. Because the reduction of Fe²⁺ to the zero valence state is not favored (E_{H} is negative), the reverse reaction is favorable. Therefore, ZVI will tend to be oxidized, passing its electrons to metal contaminants capable of existing at multiple oxidation states under standard subsurface conditions. Not all metal contaminants will participate in these types of reactions. Contaminants having E_{H} values higher than -0.44V, such as U(VI) and Cr(VI), can be reduced by the oxidation of ZVI. This material has been studied and used extensively for the reductive dechlorination of chlorinated solvents and for the reduction of Cr(VI) to Cr(III), which can form an insoluble hydroxide. Similarly UO₂²⁺ (U is in the +6 state) can be reduced to UO₂⁰, which is a solid (U is in the +4 state) (USEPA, 1998).

The University of Waterloo holds the patent for the use of ZVI to remediate contaminated groundwater reductively. The commercial rights to this material have been granted to EnviroMetals (Gavaskar *et al.*, 1998). Besides having a low E_{H} value, ZVI is favored because scrap Fe is relatively inexpensive (about \$375/ton), and is easy to obtain in large quantities (USEPA, 1998). Two U.S. suppliers provide iron filings with the following characteristics:

Table 1. Characteristics of Iron Filings. (USEPA, ITRC and RTDF, 1999)

Grain Size	2.0 to 0.25 mm (-8 to +50 mesh)
Bulk Density	2.6 g/cm ³ (160 lb/ft ³)
Specific Surface Area	1.0 m ² /g
Hydraulic Conductivity	0.05 cm/sec (142 ft/day)

Interference with reactions can occur if the groundwater is oxygenated. Oxygen (O₂) can oxidize Fe⁰ and cause FeO(OH) or Fe(OH)₃ solids to form. Besides making the Fe⁰ no longer available to interact with contaminants, the solid formation can clog the media, thus reducing hydraulic permeability. Most contaminated groundwater plumes are not highly oxygenated. However, to remove any O₂ that may be present, a pretreatment buffer zone of sand and pea gravel mixed with about 10-15% Fe⁰ by weight can be placed up-gradient of a 100% Fe⁰ reactive cell. The Fe⁰ in the pretreatment cell will reduce any O₂ to H₂O before it can reach the reactive cell. The pea gravel and sand create high permeability conditions so that any precipitates formed in the buffer zone will not interfere with groundwater flow to the barrier (Gavaskar *et al.*, 1998).

In actuality, iron granules will never be 100% Fe⁰ because of exposure to atmospheric oxygen. It is recommended, however, that they be at least a minimum of 95% Fe⁰ by weight, with the remaining 5% being oxide coatings and minor amounts of carbon. ZVI interactions with the contaminant plume raise the water's pH by producing hydroxyl (OH⁻). An increase in OH⁻ concentration can cause clogging as hydroxide and carbonate precipitates are formed. Carbonate (CO₃²⁻) exhibits acid/base behavior, becoming protonated according to pH (H₂CO₃ + OH⁻ → HCO₃⁻ + H₂O, HCO₃⁻ + OH⁻ → CO₃²⁻ + H₂O) (Gavaskar *et al.*, 1998). These protonation events

occur at the carbonate species' pKa values (pH 6 and 10.3). An increase in CO_3^{2-} can result in solid formation with Fe, Ca, and Mg, which can impede groundwater flow through the barrier. Solid precipitation can be favored when it results in the removal of toxic metals from the groundwater. However, it is detrimental if it decreases the hydraulic conductivity through the barrier or if it interferes with the dominant contaminant removal mechanisms. To remedy this problem, buffering amendments can be added to the media to keep the pH at a neutral level (Gavaskar *et al.*, 1998). Keeping a neutral pH is also beneficial to any micro-organisms that may be contributing to the remediation efforts.

1.3.1.2 Other Forms of Fe Containing Media

Chromium reduction rates by pyrite (FeS), siderite (FeCO₃), and ZVI have been laboratory tested. ZVI was found to react the fastest (USEPA, 1998). However, the other forms of Fe containing media warrant discussion. Pyrite produces acid when it is exposed to O₂ or H₂O, which could be effective in buffering the base formed by ZVI (Gavaskar *et al.*, 1998).

Bimetallic media, which consists of ZVI pellets coated with other metals, can also be considered. These coatings have been found to speed up reaction rates for organic contaminants, and have the potential to be applied to inorganic contamination scenarios. Copper acts as part of a galvanic couple with the Fe and increases electron activity. Palladium (Pd) acts as a catalyst in the ZVI-contaminant redox reaction. Similarly, Ni has the ability to increase degradation rates. A cost tradeoff becomes apparent with bimetallic reactive cells. They can be smaller, and hence cost less, because the necessary residence time is decreased. However, the additional materials may be more costly than Fe (Gavaskar *et al.*, 1998). Additionally, issues with the long-term performance of these catalysts need to be addressed (USEPA, ITRC and RTDF, 1999).

A tradeoff between surface area and porosity typically exists, as smaller particles have a greater surface area to volume ratio than larger particles, but provide for a smaller porosity because they can pack closely together. With Cercona iron foam, both high surface areas and porosities can be achieved, as the particles are not spherical and contain pore spaces. The foam is created by gelation of soluble silicates and aluminates combined with an iron aggregate under controlled conditions. These controlled conditions allow the desired form to be reproducible (Gavaskar *et al.*, 1998) so that predictive models are more accurate.

A colloidal iron particle has been developed but not yet field tested. Its 1-3 μm diameter makes it small and light enough to be mixed in a slurry and injected into a well. It has the potential to settle out of the slurry and adhere to soil particles. Its greater surface area to volume ratio allows it to be cost effective, as less media can be used (Gavaskar *et al.*, 1998).

1.3.1.3 Sodium Dithionite

Remediation with sodium dithionite (NaS₂O₄) is achieved by introducing a liquid into the subsurface in order to create a series of overlapping reaction zones. This type of emplacement encounters more regulation issues than barriers consisting of solid media do, as the injected liquid is mobile in the groundwater. This strategy has the benefit that media introduction is fairly

non-invasive to the subsurface or to any surface level activities.

Sodium dithionite has the reducing power to transform ferric oxides naturally occurring in the soils to the ferrous form ($3+ \rightarrow 2+$). The Fe^{2+} now has the ability to reduce toxic metal contaminants to innocuous or immobile forms (USEPA, 1998). However, laboratory experiments have indicated that it is only effective for easily reducible compounds, such as UO_2^{2+} (Gavaskar *et al.*, 1998). Easily reducible compounds are those with high E_H values. Contaminant reduction with the reaction zone formation technology is less effective than that utilizing ZVI because the extra electrons available to be transferred to the contaminant's reduction half-reaction from the Fe^0 to Fe^{2+} oxidation half-reaction are not produced, as this reaction does not occur. Only the Fe^{2+} to Fe^{3+} oxidation half-reaction occurs.

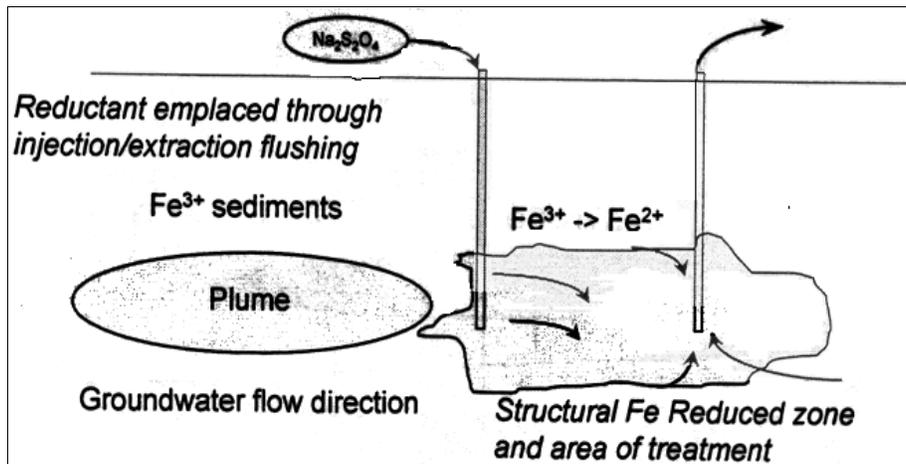


Figure 3. Injection of Sodium Dithionite (USEPA, ITRC and RTDF, 1999).

1.3.1.4 Polysulfide Compound

Instead of injecting a compound that can interact with Fe^{3+} in the subsurface, which in turn reduces metal contaminants, a reductant that directly interacts with the contaminants can be introduced to the subsurface by direct push injection or hydrofracturing. Pump and treat systems have been utilized with polysulfide (S_3^{2-} , S_4^{2-} , S_5^{2-} , S_6^{2-}) or bisulfite (HSO_3^-) compounds being injected with the clean water. The sulfur is oxidized as Cr(VI) is reduced to Cr(III) , its immobile form (Rouse, 1999).

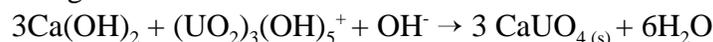
This technology has been used in full-scale applications at wood treatment sites in California and Indiana to depths of forty feet. Currently, deeper applications are being investigated. Alternatively, a picket fence arrangement of one-inch Geoprobe holes can be applied within the plume. The reductant is dripped continually into the source area and allowed to travel down-gradient with the natural groundwater flow (Rouse, 1999).

Chromate reduction has been observed as an oxyhydroxide coprecipitate. There has been concern over the ability of manganese (Mn) oxides naturally present in the subsurface to reoxidize Cr(III) to Cr(VI) , resulting in remobilization. Cores taken from Michigan soils and exposed to Cr(III) and Mn oxides resulted in reoxidation. However, those that underwent a reduction of Cr(VI) to

Cr(III) and were then flushed with Mn oxide solutions did not result in Cr reoxidation. Apparently, the Cr(III) oxyhydroxide precipitates were so tightly bound up in the soils that redox reactions with Mn oxides could not remobilize the Cr(III). Lastly, sulfates levels drop in the reactive region, as the reducing conditions created encourage the growth of SRBs (Rouse, 1999).

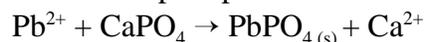
1.3.2 Precipitation Barriers

Some barriers are designed not to alter the oxidation state of the contaminant, but to provide a ligand for solid formation. Lime barriers [Ca(OH)₂] raise the pH to 12-12.5 to facilitate precipitation of metal hydroxides (NATO, 1998). Hydrated lime has the ability to remove uranium, arsenic, molybdenum, and selenium from the aqueous phase (USEPA, 1998). This is displayed by the following reaction:



(Morrison and Spangler, 1993)

Limestone (CaCO₃) has also been noted to precipitate Cr(III) into a carbonaceous solid (USEPA, 1998) and to retard the movement of Cr(III) through soil (Artiole and Fuller, 1979). Limestone acts as a pH buffer. Raising the pH can cause metal precipitation because many metals are more soluble in acidic than in basic conditions. Hydroxyapatite (CaPO₄) is moderately soluble in water and can interact with metals to form a solid precipitate as in the following example:



(USEPA, ITRC and RTDF, 1999). Historically, limestone walls have been used to control acid mine drainage.

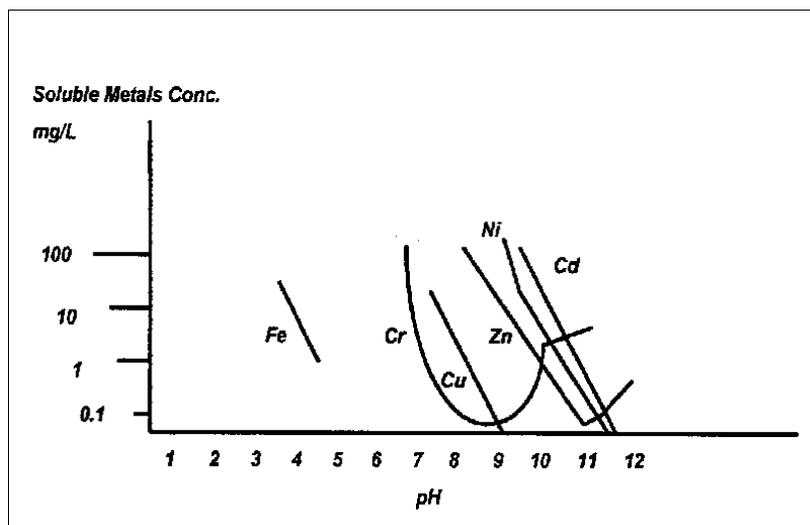


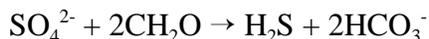
Figure 4. Metal Solubility as a Function of pH (USEPA, ITRC and RTDF, 1999).

1.3.3 Biological Barriers

PRBs can be designed to stimulate the growth and activity of naturally occurring microorganisms. Certain communities manipulate contaminants in their metabolic processes, typically

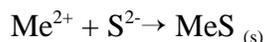
as an electron donor or TEA. Biological barriers supply a limiting resource to the microbial communities already present in the subsurface or inoculate the plume with a culture capable of transforming the contaminants. Laboratory studies have analyzed the effects of adding steel wool inoculated with *Paracoccus denitrificans* to water contaminated with NO_3^- . Denitrification occurred, so NO_3^- was reduced to N_2 gas (USEPA, 1998). The nitrogen cycle is discussed in Section 3.2.4.

Organic carbon, which is essential for building cell biomass and—in most cases—for donating electrons, typically is limiting in the subsurface. Barriers containing sugars or organic acids can stimulate SRBs to reduce SO_4^{2-} to S^{2-} by the following reaction:



(Waybrant, Blowes, and Ptacek, 1998).

Sulfides exhibit acid-base behavior. Deprotonation events occur at pHs 7.0 and 13.9, resulting in HS^- and S^{2-} . The unprotonated form, S^{2-} , participates in solid formation most frequently. Although this species is not dominant until the pH is unnaturally high (a pH this high will never really occur and would actually kill the beneficial micro-organisms.), a great enough concentration of S^{2-} will be present at ambient pH levels to facilitate solid formation (Snoeyink and Jenkins, 1980). The S^{2-} can interact with contaminant metals (Me^{2+}) to form insoluble precipitates by:



(USEPA, 1998).

A variety of organic materials have been tested to determine which best stimulate microbial sulfate reduction. Those mixtures derived from a variety of organic sources, e.g. leaves, wood chips, were found to be most effective at producing S^{2-} (Waybrant, Blowes, and Ptacek, 1998). PRBs composed of compost are currently in use to remediate abandoned mines, such as the Vancouver and Nickel Rim sites described in Section 3.2.

Micro-organisms can also be stimulated by organic carbon or hydrogen gas (H_2) to directly reduce contaminants. For example, U(VI) can act as the TEA to become reduced to U(IV), which exists as a solid in the form UO_2 (USEPA, 1998).

1.3.4 Sorption Barriers

PRBs can also be designed with materials that attract and sorb groundwater contaminants. These include granular activated carbon, bone char, phosphates, zeolites, coal, peat, and synthetic resins (USEPA, ITRC, and RTDF, 1999). This interaction is not as permanent as a solid precipitation reaction and is highly dependent on subsurface conditions, especially pH (Morrison and Spangler, 1993).

1.3.4.1 Surfactant Modified Zeolites (SMZ)

Because soil solids are predominantly negatively charged, cationic contaminants can be attracted

by electrostatics. However, some contaminants, such as Cr and As, exist as oxyanions (such as $\text{Cr}_2\text{O}_7^{2-}$ and AsO_4^{3-}), which are repelled by a soil's cation exchange sites (Sparks, 1995). Researchers at New Mexico Tech and the Oregon Graduate Institute have been conducting pilot scale tests on solids capable of sorbing both anionic and cationic metal contaminants.

Zeolites are naturally occurring aluminosilicates with a cage-like structure. They have been used extensively in the wastewater treatment arena to remove cationic contaminants. The zeolite's surface can be modified by the addition of a high molecular weight amine, such as hexadecyltrimethylammonium (HDTMA). These molecules exchange irreversibly with cations on the zeolite surface, but are too large to access the internal sites. HDTMA consists of an organic tail and a positively charged head. Organic contaminants sorb to the tail by hydrophobic partitioning, as oxyanionic contaminants are attracted to the positive head by electrostatic interactions. Cationic contaminants can sorb to the zeolite's internal cation exchange sites (Bowman *et al.*, 1999a; Roy, 1999).

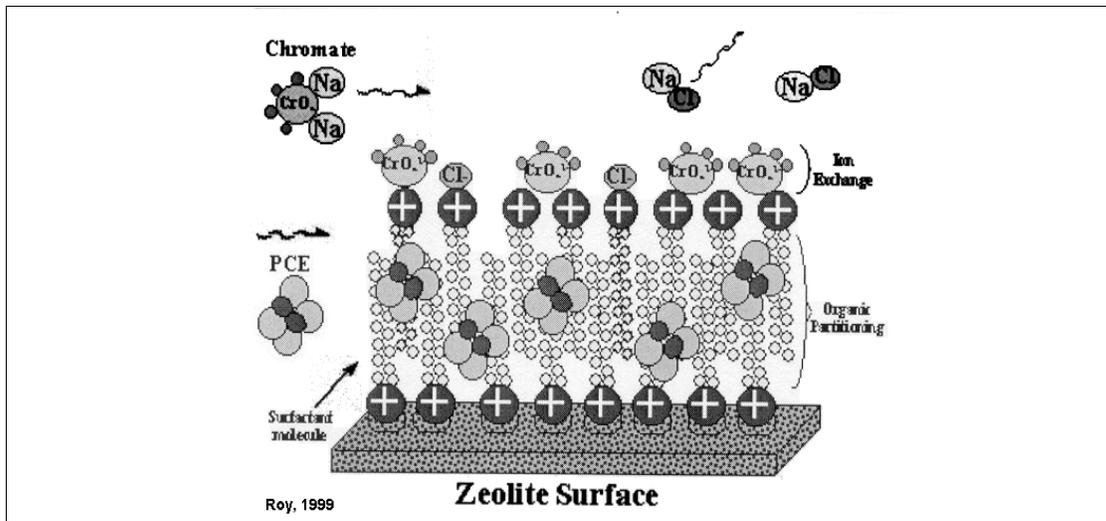


Figure 5. HDTMA Bromide (Roy, 1999).

Surfactant modified zeolites (SMZ) costs average about \$425/ton, which includes zeolites, surfactants, and processing. Because the zeolite is very porous, having a specific gravity of 0.9, the cost per unit volume (\$12/cubic foot) is very low (Roy, 1999). This medium had been pilot tested at the Large Experimental Aquifer Program (LEAP) tank in Oregon. A mixed waste of TCE and Cr was applied to the tank. A retardation factor (which is the contaminant's velocity in sand divided by its velocity through the SMZ) of 44 was achieved for Cr (Bowman *et al.*, 1999a).

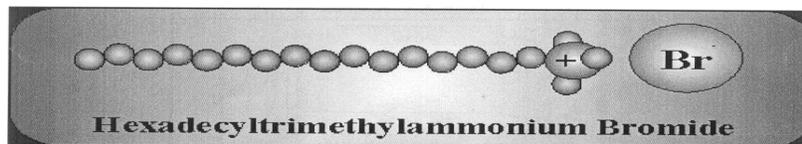


Figure 6. SMZ Schematic

1.3.4.2 Forager Sponge

The Forager Sponge technology was accepted into the Superfund Innovative Technology Evaluation (SITE) Program in June 1991 and demonstrated at the National Lead Industry site in Pedricktown, NJ in April 1994. It is an open-celled cellulose housing iminodiacetic acid groups which chelate transition metal cations by cation exchange processes in the following affinity sequence: $Cd^{2+} > Cu^{2+} > Hg^{2+} > Pb^{2+} > Au^{3+} > Zn^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} > Al^{3+}$.

The sponge polymer also contains tertiary amine salt groups that can bind anionic contaminants, such as the chromate, arsenic, and uranium oxide species. It can be designed for site specific needs to contain a cation that forms a highly insoluble solid with the anion of interest. For example, Fe^{3+} pre-saturation can be performed so that formation of insoluble ferric arsenate solids occurs. Absorbed ions can be eluted from the sponge so that it can be recharged. A series of sponges can be placed vertically in wells or horizontally in trenches (Dynaphore, 1999).

1.4 Treatment Configurations

In most cases, reactive media has been applied to the subsurface in one of two basic barrier configurations: continuous or funnel and gate. Both are applicable for rather shallow plumes (50-70 feet deep) (USEPA, 1998). In both cases, the barrier can be keyed into the aquitard to prevent plume migration below the reactive zone or can be hanging if the contaminant plume is fairly shallow or the aquitard is very deep (Gavaskar *et al.*, 1998).

1.4.1 Continuous Wall

With this configuration, reactive media is placed across the entire plume. Its orientation is such that all of the contaminated groundwater will flow through it. In order for the plume to not be diverted around the reactive zone, its permeability must be equal to or greater than that of the aquifer. It is recommended that it be at least twice that of the subsurface so that any precipitation that occurs will not disrupt groundwater flow through the media (USEPA, 1998).

Continuous barriers have been used at most sites. In their simplest form, they are excavated trenches filled in with granular Fe (other media can be added, but Fe has been used the most). The trench excavation and media properties should be such that groundwater flow is not disrupted. Because this is a passive technology, remediation relies on the natural movement of contaminated groundwater through the reactive media. The fact that the barrier must be placed below the water table presents the problem of water intrusion or trench collapse during media installation. Temporary sheet piling, a degradable grout, a continuous trenching machine, or an innovative emplacement method must usually be employed in installation operations (USEPA, 1998). Installation techniques are described in more detail in Section 2.2.

1.4.2 Funnel and Gate

This arrangement consists of an impermeable material that diverts contaminated groundwater through a reactive gate (USEPA, 1998). A wall of sheet piling or a slurry trench cutoff wall acts

to converge heterogeneous hydraulic flows and homogenize contaminants into a high conductivity cell or series of cells (Gavaskar *et al.*, 1998; Starr and Cherry, 1993). Several configurations can be utilized. A straight wall can be interspersed with multiple reactive gates. A “V” shaped wall can be fitted with a gate at the apex so that the plume is funneled through the reactive area. A “U”-shaped wall can partially surround the plume and source area. The up-gradient side of the source can be surrounded by the wall so that clean water does not flow into it. This reduces the volume of contaminated water to be treated and increases the plume’s residence time in the gate by preventing an influx of clean water from pushing the plume through the reactive area (Starr and Cherry, 1993).

A funnel and gate system using sheet piling for the funnel component may be superior to the continuous trench because less materials can be used and less soil needs to be excavated (USEPA, 1998). The minimum volume of reactive media needed does not depend upon which configuration is used, but funnel and gate systems may be less expensive because:

- Continuous trenches require media to be spread across entire plume, while funnel and gate systems localize media in the gate area. Less expensive materials, such as sheet piling, are used for the rest of the system. The overall wall system is usually larger for a funnel and gate, but the amount of reactive media used is usually less.
- Media in a localized gate is easier to maintain than that spread across a large trench.
- Monitoring costs are lower as a smaller down-gradient area is created.
- Influent contaminant concentrations can be homogenized by upstream mixing so that reactive materials are not wasted on areas of low contaminant concentration (IBC, 1999).

Steel sheet piling typically is used to form the funnel section. It is very durable and maintains its shape during emplacement. Depending on dissolved oxygen levels in the groundwater and the corrosivity of the contaminants, it has a life expectancy of anywhere between seven and forty years. Pieces are usually 40 feet long, but can be welded together in order to construct longer walls. They can be driven about 80 feet deep but tend to deviate from vertical around 60 feet deep. The pilings must be placed deep enough so that contaminated water does not flow under them. Leakage can be a problem at welded areas. To remedy this, the University of Waterloo has developed pilings with sealable joints. The joints fit together to connect walls and are filled with grout to prevent leaking. Care must be taken during installation so that the joints are not damaged by friction. Additionally, the pilings have limited availability, as they are only manufactured in Canada (Gavaskar *et al.*, 1998).

The impermeable sections of the funnel and gate system can also be constructed from slurry walls. A soil-bentonite mixture is the most common type used. It is the cheapest to install, has a low permeability, and is chemically stable. Some of the excavated soil from the trench is mixed with the bentonite above ground. Therefore, adequate space is required for the storage and mixing of this soil. The empty trench is then filled with the mixture, which must be fluid enough to uniformly flow down the trench slope without creating pockets of high permeability (Gavaskar

et al., 1998).

Cement-bentonite slurry walls have greater strength than those containing soils and can be applied in areas of extreme topography. However, cement is more expensive to use and has a higher permeability than soil. Because excavated soil is not used in the wall, it all must be disposed of, which increases installation costs. But this type of wall is suitable for sites having limited ground space, as an area to mix the slurry is not needed (Gavaskar *et al.*, 1998).

Composite barrier walls are based on a variation of the above impermeable barriers. These walls, which are composed of a mixture of water, bentonite, cement and an aggregate that hardens yet remains flexible can be utilized when both strength and deformability are needed. They have a very low permeability and are chemically stable. During installation, temporary paneled bentonite wall sections are placed on the plume side of the barrier. The plastic concrete is then poured with a tremie tube into the excavated trench to replace the bentonite (Gavaskar *et al.*, 1998).

1.4.3 Alternative Configuration: the GeoSiphon/GeoFlow Cells

Westinghouse Savannah River Company has patented a system that utilizes the natural hydraulic head difference between two points to induce groundwater flow. The plume flows from areas of high pressure at the source to low pressure discharge points in the subsurface, into surface water, or at the ground surface. The head difference is enhanced by a large diameter well connected to a siphon (GeoSiphon) or to an open channel (GeoFlow) which empties into an outfall ditch. The technology is still passive, but the induced flow allows remediation to progress much faster than with the above configurations. The media cells can be placed anywhere along the flow path, can be removable or permanent, can contain any reactive material, and can be *in situ* or *ex situ*. Depth of installation is only limited by available equipment. It was first installed by the Auger and Caisson method at the TNX Savannah River site in July, 1997 to treat chlorinated solvents (Cardoso-Neto *et al.*, 1999; RTDF, 1998).

1.5 Advantages of PRB Use Over Conventional Technologies

Pump and treat is the most commonly used technology for treating contaminated groundwater at Superfund sites. Even though it is widely used, it is not the most effective option for remediating subsurface contamination. It is very costly and highly energy. Collective cost savings from using PRBs over pump and treat methods may range from \$500 million to greater than \$1 billion (USEPA, ITRC, and RTDF, 1999).

Non-aqueous phase liquids (NAPLs) and species sorbed to the soil matrix can be left behind by pump and treat operations. As clean water enters the contaminated area, the subsurface re-equilibrates according to each constituent's partition coefficients. This typically results in sorbed pollutants or those in the NAPL layer being driven by a concentration gradient into the clean water. The groundwater is then recontaminated and must be pumped out and retreated. This series of events can continue as long as NAPLs or sorbed contaminants remain.

PRBs have the advantage in that they can act on some NAPLs (Starr and Cherry, 1993). Light

NAPLs (LNAPLs) float and can move with the groundwater. Dense NAPLs (DNAPLs) sink and move with or slower than the groundwater can passively flow through the reactive media. However, some NAPLs move so slowly that they are considered immobile. They will not be treated by the PRB if they do not move through its media. In this instance, a PRB offers no remediation advantage over pump and treat methods.

Because PRBs are passive, meaning that they are designed to function for a long time with little or no energy input, a potential cost reduction of greater than 30% can be achieved by using PRBs instead of pump and treat. Pump and treat can cost \$12-14 million, while a typical PRB costs \$400,000 (NATO, 1998). Costs are low because there are no operating expenses except for regulatory compliance or monitoring that may be needed (USEPA, 1998). Additional operating costs will be incurred if the media loses reactivity or permeability over time and must be replaced, which is likely to occur over a long operating time (RTDF, 1998).

PRBs are also succeeding because they are unique in that they can treat wastes that are both heterogeneous in composition and concentrations. There are much data available and being documented, which makes implementation and decision making easier (IBC, 1999). Lastly, because PRBs require no above ground equipment, except monitoring devices, the property can be returned to economic use during remediation (Gavaskar *et al.*, 1998). Typically paved surfaces, such as parking lots, cover PRBs. This prevents rain water from infiltrating into the plume and, consequently, increasing the volume of water requiring treatment.

1.6 Potential Limitations

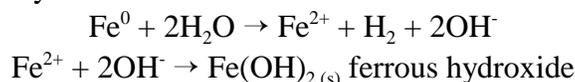
A notable shortcoming of the use of PRBs is that remediation is a lengthy process. Because the technology relies on the groundwater's natural movement, aquifers with low hydraulic conductivities can require great periods of time to be remediated (ITRC, 1998). Additionally, the barrier is permanent. It cannot treat contamination up-gradient of itself. Only that part of the plume that moves through the media can be remediated. Typically, the contaminant source or center of mass is immobile. It and any portions of the plume that do not move through the barrier must rely on natural attenuation or other treatment methods to be cleaned. Additionally, the PRB cannot be moved if the plume's movements deviate from what models had predicted. Therefore, a thorough characterization of the plume's behavior must be made prior to installation (Gavaskar *et al.*, 1998).

Proper design parameters must be carefully identified during the characterization phase because there really are no operating parameters that can be adjusted during the performance of this passive system. Therefore, the wall must be sized correctly to respond to any subsurface changes. For example, it must not deal only with the parent compounds of interest, but must be designed to treat any toxic transformation products that are created (USEPA, 1998). Nitrate (NO_3^-) reduction to N_2 gas proceeds in steps as the nitrogen is reduced from +5 to 0 oxidation states. Nitrite (NO_2^-) is the first transformation product in the denitrification process. It is highly water soluble, mobile, and very toxic. Therefore, designers cannot only size the reactive media to remove the contaminants of interest from the groundwater, but must also consider any toxic transformation products.

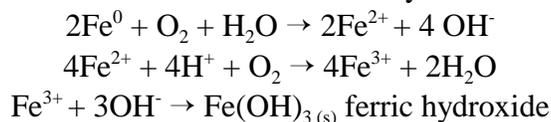
Another toxicity issue arises with the treatment of radionuclides. Barriers that facilitate sorption or precipitation cause contaminants to be concentrated in the area of the reactive media. Above-ground receptors do not come into contact with these concentrated contaminants as long as the soils are undisturbed. However, radionuclides emit some forms of radiation that can penetrate the soil matrix. Does concentrating this activity in the wall present a threat to receptors in the vicinity of the site? This question remains unanswered (ITRC, 1998) as many walls are young and many radionuclide contaminated sites are in remote areas. It also remains unknown whether a concentration of metals or radionuclides presents a threat to subterrestrial biota, such as micro-organisms and macro-invertebrates. However, the benefits of removing these constituents from the groundwater most likely outweigh any concerns incurred by concentrating them as solids.

A barrier's performance can be compromised if reactivity or permeability is lost. A large reservoir of Fe, a favorable pH, and an available substrate can promote the activity of the SRBs present and any methanogens [bacteria that reduce carbon dioxide (CO₂) to methane (CH₄)] in the subsurface. This can result in a rapid corrosion of the barrier, a build-up of precipitates, and biofouling (a build-up of biomass that restricts water flow) (RTDF, 1998).

As Fe⁰ is oxidized, ferrous hydroxides are formed.



If O₂ is present, Fe²⁺ is further oxidized to Fe³⁺ and ferric hydroxides are formed.



Ferrous hydroxides exist as magnetite coatings that likely do not restrict flow, but the ferric hydroxides are precipitates that can clog the media (USEPA, 1998). One method used to avoid clogging is to make the media more permeable than the aquifer so that any precipitation that occurs will not impede groundwater flow through the reactive cell (IBC, 1999). Colloidal loss of fine particles from the wall can occur with water movement. This can possibly counteract the effects of precipitation and keep permeability high. However, if contaminants sorb to these colloids they can be spread further and faster than if they were just dissolved in the groundwater (RTDF, 1998). A filter layer can be applied up-gradient to prevent fine grain inflow into the reactive area (NATO, 1998). An up-gradient filter can also remove any dissolved O₂, as was discussed earlier in Section 1.4.1.1 on ZVI. Designing permanent, accessible spacings for refilling/replacing clogged media and seals for rain water and air tightness into the barrier can also help to deter problems associated with precipitate formation (Beitinger *et al.*, 1998).

Biofouling is suspected to be a potential problem when reactive media manipulates the subsurface conditions so that microbial growth is promoted. However, the high pH created by Fe corrosion discourages growth. No problems with excessive biomass have been reported in bench top laboratory analysis or in the field thus far (USEPA, 1998).

2 Site Characterization and Design Parameters

When assessing site conditions to determine the feasibility of using a PRB, four general subsurface properties must be measured: plume characteristics, hydrogeology, geochemistry, and microbial activity. Typically, wells are installed for sampling. But push technologies, which are quicker and cheaper, are becoming available. They can be used to assess several depths along a vertical axis in order for the plume can be more fully characterized (USEPA, 1998).

2.1 Site Characterization and Design

2.1.1 Plume Characteristics

Concentrations and spatial distributions of contaminants must be fully characterized so that the barrier can be positioned to treat the entire plume. Predictions must be made about the plume's future movements. Knowledge of vertical distribution is essential so that the contamination cannot flow over or under the reactive area or so that money is not lost as the barrier is sized too large. The barrier is installed down-gradient from the plume's center of mass (USEPA, 1998). It must be determined whether the center of mass is moving and if it will reach the barrier. Is natural attenuation occurring at the source so that only low contaminant concentrations reach the reactive area? This must be well-characterized, so that the media can be sized to treat the greatest contaminant concentrations that can reach it (USEPA, ITRC, and RTDF, 1999).

The behavior of the plume's constituents must also be characterized. As some transformation products are toxic, the barrier must be designed to treat these compounds. Therefore, an understanding of not only what contaminants are in the plume, but also of their chemical properties is essential for properly determining the necessary residence time (IBC, 1999). When radionuclides are present, radiation is of concern. Therefore, isotopic analysis and gross alpha and beta counts are needed for a thorough plume characterization (ITRC, 1998).

2.1.2 Hydrogeology

Because the system is passive, all of the contamination must reach the barrier by natural groundwater flow. Therefore, hydraulic determination is the most important part of site characterization (USEPA, ITRC, and RTDF, 1999). Porosity, conductivity, and the effects of any pumping near the site must be taken into account. Seasonal changes and recharges must also be considered as plume behavior can fluctuate as subsurface conditions vary (USEPA, 1998). Previously recorded field data is usually available for determining seasonal water level fluctuations (IBC, 1999). Barriers are usually placed at least two feet above the water table to

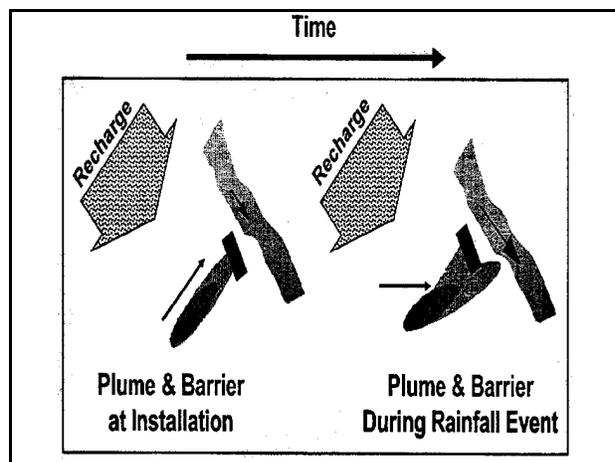


Figure 7. Seasonal Recharge Events Can Cause the Plume to Bypass the Barrier (USEPA, ITRC and RTDF, 1999).

account for these fluctuations (Gavaskar *et al.*, 1998).

Depth to bedrock and the presence of any large impermeable rocks will affect barrier placement. Large rocks that are not located prior to installation can prove costly if the barrier cannot be placed where excavation has begun or if equipment is damaged during installation operations. A barrier can be hanging if the plume is shallow and the aquitard is too deep to economically reach (USEPA, 1998). However, it often must be keyed at least one foot (Gavaskar *et al.*, 1998) into the bedrock to prevent underflow. Any fractures in the impermeable layer must be identified and sealed so that contaminant escape cannot occur (USEPA, 1998). Alternatively, a geotextile fabric or concrete layer can be applied horizontally under the PRB to prevent underflow (Gavaskar *et al.*, 1998).

The hydraulic gradient, which is the change in hydraulic head over a distance, can be determined in all three dimensions. Vertical determinations of the gradient can give an indication if underflow could pose a problem. Percent porosity, or pore space, also can be used to model flow patterns and can be calculated by the following equation (Gavaskar *et al.*, 1998):

$$\% \text{ porosity} = 100\% [1 - \text{bulk density} / \text{particle density}].$$

Bulk density is the mass of solids divided by a volume of soil matrix. This volume includes soil solids and pore spaces. The soil is dried so that all of the mass is from solids and not from water. Particle density is that same mass of solids compressed so that there are no pore spaces. It is the solid's mass divided by the solid volume. It is approximately 2.65 g/cm³ for typical soils. This calculation can be used for developing a medium of a desired porosity.

2.1.3 Geochemistry

To maximize a barrier's performance and foresee any possible troubles, geochemical measurements must be taken. These include pH, dissolved O₂, E_H, carbonate alkalinity, and concentrations of species that can react in the conditions created by the media. These can include SO₄²⁻, Ca, Fe, Mg, Mn, Al, Ba, Cl, F, CO₃²⁻ (and its protonated species) (USEPA, 1998). Many of these species are important because they can affect precipitate formation, which can decrease reactivity by coating available surfaces and can lower permeability by clogging pore spaces. For example, calcite (CaCO₃) or siderite (FeCO₃) buildup can occur if concentrations of Ca, dissolved Fe, or CO₃²⁻ are high. pH can affect the amount of CO₃²⁻ available for solid formation because it exhibits acid-base behavior. Dissolved O₂ can cause ferric hydroxide precipitate formation. If the area is anoxic, then ferrous hydroxides will dominate, which do not cause clogging problems (USEPA, 1998). Precipitate buildup is of importance because it can decrease permeability. This forces groundwater to flow through a smaller pore volume, which increases velocity and lowers residence time. This could result in contaminant break-through (USEPA, ITRC, and RTDF, 1999). Conductance, salinity, and turbidity measurements are also important (ITRC, 1998). Turbidity can be an indication of colloids or microbial communities. Colloids can be problematic if contaminants sorb to them and are carried down-gradient of the barrier.

2.1.4 Microbial Activity

Microbial communities can participate in complex interactions in the reactive zone. Many aspects of their role in remediation with PRBs have not yet been elucidated. They can be detrimental to the barrier's performance if their overgrowth causes plugging. Phospholipid fatty acid analyses can be performed to determine the reactive area's potential for biofouling (USEPA, ITRC and RTDF, 1999). Conversely, micro-organisms can perform many beneficial roles. SRBs reduce SO_4^{2-} to S^{2-} so that insoluble metal sulfides can be formed (USEPA, 1998). This is a significant removal mechanism for contaminant metal cations.

2.1.5 Sampling Methods

Conventional characterization methods include soil borings, soil gas surveys, shallow groundwater surveys, and the use of monitoring wells. Innovative techniques, such as direct push tools, ground-penetrating radar, seismics, and hydro-geochemical mapping, are increasingly being applied. Push tools, such as Geoprobe and Hydropunch, can be used more rapidly and inexpensively than traditional borings. Therefore, a denser sampling array of the plume can be utilized to better characterize the subsurface heterogeneity. Discrete vertical delineation of the aquifer can also be obtained (USEPA, ITRC, and RTDF, 1999).

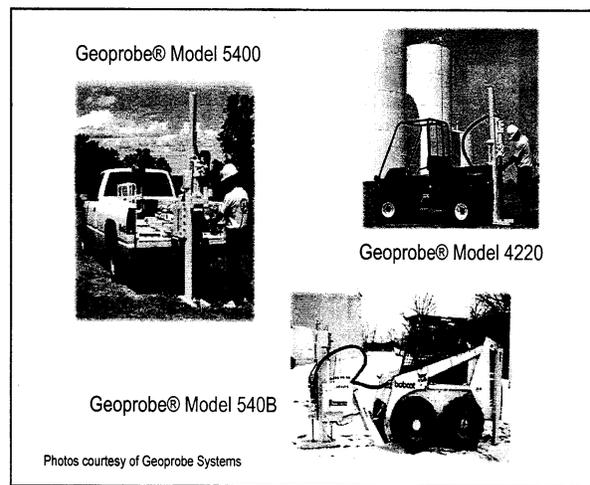


Figure 8. Examples of Geoprobe Sampling Devices (USEPA, ITRC and RTDF, 1999).

Radar and seismics can be used to ascertain bedrock and water table depth and to locate any buried objects. Flow models can be utilized to predict the influence of hanging walls or of various funnel and gate configurations on groundwater flow (USEPA, ITRC, and RTDF, 1999).

2.1.6 Sizing/Design Parameters

Barriers must be designed to be site specific. So that they can respond to the unique characteristics of each site, all of the aforementioned parameters and issues must be taken into account. Plume characterization will reveal

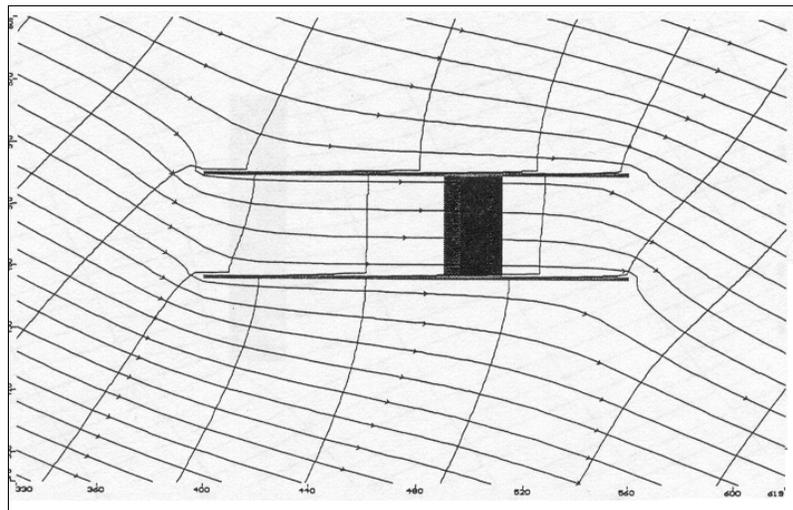


Figure 9. Representative Flow Lines Modeled for a Modified Gate Design (USEPA, ITRC and RTDF, 1999).

that concentrations are not consistent across a cross sectional area. Because it is difficult to vary media thickness along the barrier, it is usually sized for the greatest concentration expected to be encountered and for the contaminant requiring the longest residence time (USEPA, 1998). Alternatives to using the thickest wall necessary along the entire plume front include placing reactor cells in series (more cells are placed where greater residence times are required), varying the media to inert materials ratios for walls mixed with pea gravel, sand, or other nonreactive solids, and homogenizing the up stream plume (IBC, 1999). This can be accomplished by surrounding the up-gradient side of the reactive cell with pea gravel, which enhances mixing. If also applied to the down-gradient side of the media, it provides a uniform environment for monitoring so that measurements are more representative of the outflow (Gavaskar *et al.*, 1998).

Sizing for hydraulics constitutes the main design emphasis in PRB engineering. A velocity through the media is first calculated. For a continuous barrier the following equation can be used:

$$V = ki/n$$

where V is velocity (length/time), k is hydraulic conductivity (length/time), i is the hydraulic gradient (unitless), and n is the porosity (unitless). Measurements of hydraulic conductivity can vary greatly within the area of interest. Therefore, to properly size the reactive area thickness and to ensure a margin of safety, the largest conductivity must be used. This results in the fastest velocity (USEPA, ITRC and RTDF, 1999).

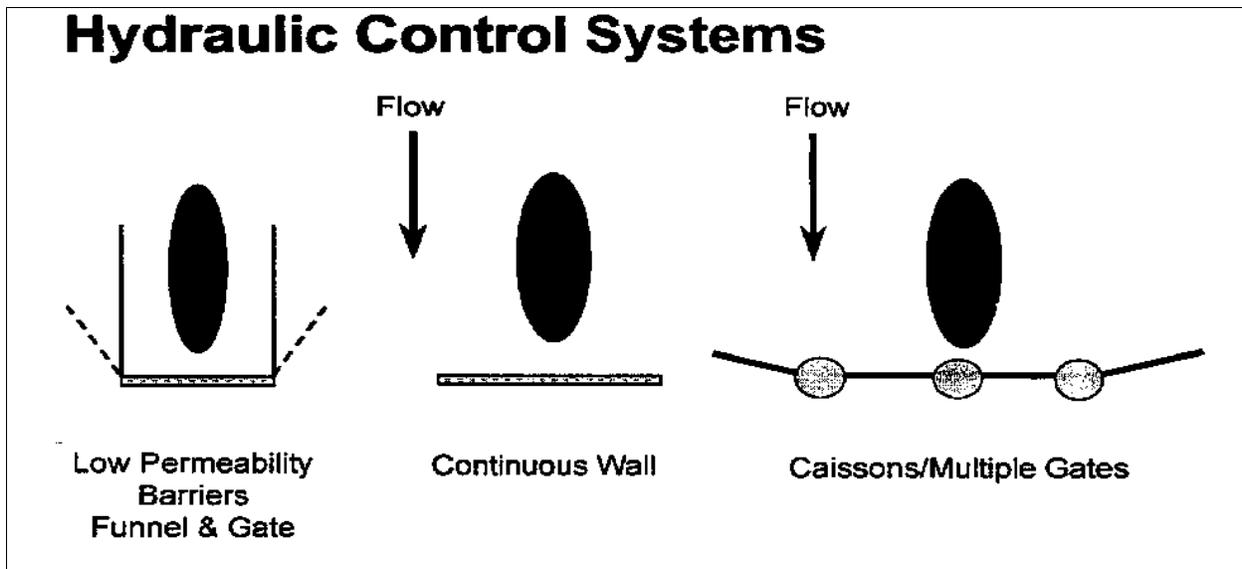


Figure 10. Sizing for Hydraulics Depends Upon Barrier Type (USEPA, ITRC, and RTDF, 1999).

If a funnel and gate is to be installed, the calculations will not be quite as straight forward, as the influence of the funnels will increase the plume's velocity. The gate(s) will be much thicker than a continuous wall, but much shorter, so that similar volumes are used to treat a given plume type. The residence time needed for the most recalcitrant contaminant, the groundwater velocity and the capture zone factor into the amount of media needed, which is independent of whether a funnel and gate or a continuous wall is installed (USEPA, ITRC, and RTDF, 1999).

However, with a funnel and gate, less media is usually used. This is because the entire length of the continuous wall has the same thickness, which was sized for the greatest concentrations of the least degradable contaminant moving at the greatest velocity. Edges of the wall will most likely encounter smaller contaminant threats and will, hence, be oversized. With the funnel and gate, each gate can be sized to the appropriate thickness so that excess media is not installed. However, the overall size of a funnel and gate system is typically larger than that for a continuous trench. Therefore, the benefit of using less media may be overshadowed by the cost of building a larger system.

Residence times (t_{res}) needed are dependent upon transformation kinetics. First order decay equations have been used to determine contaminant degradation (IBC, 1999; USEPA, ITRC, and RTDF, 1999):

$$C_t = C_0 e^{-\lambda t},$$

where C_t is concentration at time t , C_0 is the initial concentration, λ is a rate constant, and t is time. The units of t depend upon the units of λ . Time units can range from seconds for bench scale tests to years for very slowly degradable compounds in field applications. The contaminant's half life ($t_{1/2}$), which is the time required for it to degrade to half of its original concentration, is equal to:

$$\ln 2 / \lambda.$$

λ can be calculated in laboratory experiments by:

$$\begin{aligned} \lambda &= -[\ln (C/C_0)] / t \\ &= \ln 2 / t_{1/2} \end{aligned}$$

Residence time is dependent upon the desired contaminant concentration. Because the decay is exponential, it will take much less time for 50% degradation to occur than for 90% to occur. However, barriers usually are sized to achieve maximum concentration limits (MCL). Residence time is calculated by:

$$t = [\ln (C/C_0)] / -\lambda$$

The groundwater flow velocity (length/time) can then be multiplied by the residence time in order to calculate the minimum media thickness needed (USEPA, ITRC, and RTDF, 1999).

However, because the subsurface and the barrier properties are heterogeneous, a safety factor should be included when sizing the reactive cell so that fluctuations are accounted for (USEPA, 1998). Some sources recommend that the media's permeability be about ten times that of the aquifer because events, such as settling of fine grained particles, solid precipitation, and biofouling, can reduce permeability over time (NATO, 1998). A media permeability greater than that of the aquifer will cause water to flow faster through the media than it naturally flows in the subsurface. This is especially true with the funnel and gate configuration, where a wide plume is channeled through a small area. The subsurface returns to its background permeability down-gradient from the gate. A potential for backup as a pressure difference builds across the reactive area is created (USEPA, 1998). Pressure backup has not posed a problem in existing barriers

because the water can spread in all three dimensions after exiting the gate. However, these increased flow rates and pressure differences must be taken into account when sizing the reactor's width so that the contaminant's residence time is sufficient.

Extrapolation from the laboratory to the field is safe when sizing for barriers that do not rely on biological reactions. However, temperature and nutrient availability vary in the subsurface so that additional safety factors must be utilized when designing for biologically mediated reactions (USEPA, 1998).

Design options for long term maintenance and monitoring can also be included in the characterization phase. PRBs can be built with openings for media replacement, with a pipe system for air or water injection in order to wash out precipitates or mix the media, and with access points for inspecting and sampling the media (NATO, 1998).

Preventative measures, which extend a barrier's lifetime, should be considered also. These are usually less expensive and less time consuming than rejuvenating the media after it has lost reactivity or permeability. For example, buffering materials can be applied at both the up- and down-gradient sides of the reactive cell. This prevents the pH from rising as much as it naturally would from Fe corrosion. A higher pH allows more of the carbonates in the system to exist in the unprotonated state (CO_3^{2-}) and produce carbonate precipitates. Buffering keeps the pH closer to neutral and, thus, prevents precipitates from forming and reducing permeability (USEPA, ITRC, and RTDF, 1999).

These manipulations will add to the materials and installation cost, but may save money in the long term if they increase the barrier's longevity. Basic material costs can be calculated by multiplying the cross sectional area of the plume by the media cost per weight by the weight needed per plume area:

$$\text{Cost} = (\text{plume X area}) \times (\$/\text{weight}) \times (\text{weight}/\text{X area}).$$

Media installation costs can be calculated by multiplying the cross sectional area of the plume by the installation cost per media volume by the media mass per cross sectional area by the inverse of the media's bulk density (USEPA, 1998):

$$\text{Cost} = (\text{plume X area}) \times (\$/\text{volume}) \times (\text{mass}/\text{X area}) \times (\text{volume}/\text{mass})$$

Alternatively, media costs can be calculated by multiplying the barrier thickness (derived as the product of velocity and residence time) by the plume's saturated thickness (range of depths the contamination inhabits) by the plume's length to obtain a volume of media required. For Fe, this volume is then multiplied by bulk density and price per ton (USEPA, ITRC and RTDF, 1999):

$$\text{Cost} = (\text{cubic volume}) \times (0.08 \text{ tons/cubic foot}) \times (\$425/\text{ton})$$

These are general calculations just for media costs. When using a funnel and gate, costs for the funnel section will have to be included. Additional costs will be incurred during the installation

process and are addressed in the following section.

2.2 Installation

Properties of the subsurface detected during the site characterization will shape the installation decision making process. Considerations for choosing emplacement techniques include: depth, media permeability, topography, site access, geotechnical constraints, soil characteristics (when serving as backfill), disposal requirements of contaminated trench spoils, available equipment, regulations, and costs. Limited site access may require a barrier to be placed directly in the plume. This may raise costs as additional safety precautions will need to be taken (Gavaskar *et al.*, 1998). Excavating in the plume can cause equipment surfaces to become contaminated. Contaminated water that is generated from cleaning machinery, along with any contaminated soils and water that are removed during excavation, will need to be safely disposed of if they cannot be treated on site. These disposal costs must also be considered in the remediation budget (ITRC, 1998).

Plume depth also affects costs. Typical trenching operations are limited to depths of twenty-five feet before costs become too high to use conventional equipment (NATO, 1998). Shallow trenches tend not to cave in before they are back-filled, while deeper ones require temporary structural walls or slurries to hold their walls up. This can be executed by driving sheet piling into the ground in a rectangular shape, excavating the soil out of the interior of the rectangle, using pumps to extract any water that flows in, filling the area with the reactive media, and then removing the pilings (USEPA, 1998). Because the sheet pilings do not act as barriers to water, extra cost is incurred for pumping out water from trenches in wet soils below the water table (Gavaskar *et al.*, 1998).

2.2.1 Conventional Emplacement

Most excavations are performed with backhoes. They provide the cheapest and fastest method and can dig down to about thirty feet deep. Up to eighty feet in depth can be reached if the equipment is lengthened with a dipper stick or if it is placed down in a hole. However, this can be expensive and time consuming. A crane with a clamshell can reach depths of 200 feet, but is slower than the backhoe and may require personnel to enter the trench to remove soils that the equipment cannot reach (Gavaskar *et al.*, 1998).

2.2.2 Continuous Trencher

To avoid the problems with trenches caving in, a continuous trenching machine, which is similar to a “Ditch Witch” can be used. It cuts open a twelve to thirty-six inch wide hole and holds it open with a trench box on a chain saw belt-type mechanism. A hopper at the top feeds media into the hollow box as it moves down. Depths of twenty to thirty feet can be achieved. The continuous trenching machine was first used in Elizabeth City, North Carolina, in June 1996. A 150' x 2' x 24' PRB was installed in less than 8 hours (USEPA, 1998).

This machinery has the advantage that it does not require workers to be placed in confined

spaces. The only health and safety issue arises with the nuisance dust from the granular iron. A simple dust mask remedies this problem. The drawbacks are that the machine is prone to break down and that it was difficult to keep track of the volume of media used (USEPA, 1998; USEPA, ITRC, and RTDF, 1999). Additionally, this type of equipment is harder to obtain than the conventional backhoes and cranes.

A variation of the standard continuous trencher has a two compartment hopper. One compartment houses the media, while the other has a roll of high density polyethylene (HDPE) liner that can be continuously unrolled and placed in the trench, if needed. Both this style and the standard machine create little spoils, produce minimal soil disturbance, do not require dewatering pumps, and are suitable for sites with limited access. However, they have trouble with wet, unconsolidated soils. Costs of using trenchers range from five to twelve dollars per square foot of wall face (Gavaskar *et al.*, 1998).

The continuous trencher can be used to install either continuous PRBs or funnel and gate systems. Typical gate installations involve extensive confined space entry for installation personnel so that it is the most expensive part of emplacement of this system. Therefore, alternative installation methods, such as the use of caissons or biodegradable slurries, are increasingly being used (USEPA, 1998).

2.2.3 Caisson

Researchers at the University of Waterloo hold a patent for a removable caisson driven funnel and gate emplacement technique (NATO, 1998). A hollow enclosure eight feet or less in diameter is vibrated or pushed down into the soil. Solids are excavated from the center before reactive media is filled in. The caisson is then pulled straight out. Multiple, overlapping installations can be utilized to build the appropriate size gate. This technique has the advantage that no trench dewatering, temporary sheet piling, nor confined space entry are required (Gavaskar *et al.*, 1998). Costs can range from \$20-\$100 per square foot (NATO, 1998).

2.2.4 Tremie Tube

A similar method, the tremie tube or mandrel, consists of a hollow rectangle filled with media attached to a drive shoe. The unit is forced down by hydrostatic force or with a vibratory hammer. The media and shoe are left in the subsurface, as the tube is drawn out (Gavaskar *et al.*, 1998; USEPA, 1998). The tube can be emplaced into the ground with any type of sheet pile driving equipment, such as a vibratory hammer or a pile driver, without mixing with the soil (USEPA, ITRC, and RTDF, 1999). No spoils are created, and the technology is inexpensive (about \$7 per square foot including labor and equipment). However, soil compaction around the reactive zone can occur, reducing permeability, and the

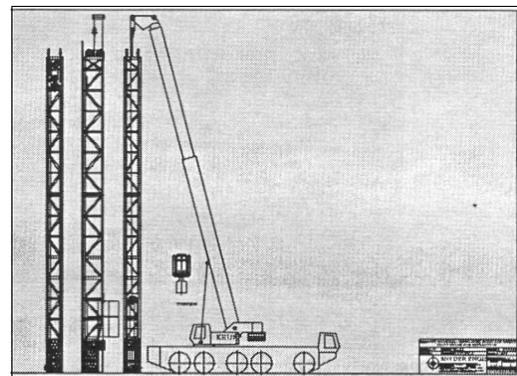


Figure 11. Installation of Tremie Tube (USEPA, ITRC and RTDF, 1999).

mandrel can be deviated off the installation path by subsurface obstructions (Gavaskar *et al.*, 1998).

2.2.5 Jetting

Nonreactive zones of the media slurry sometimes occur with conventional installation. To avoid this, high-pressure jetting can be used. It has been used for the injection of grouting in construction operations and for impermeable barrier emplacement (USEPA, 1998). This technology is being shifted from being solely used in civil engineering applications to being applicable in the environmental remediation arena (USEPA, ITRC, and RTDF, 1999).

This technology can be applied to PRB installation with a slurry of small iron particles. Jetting nozzles can spray a colloidal slurry under high pressures (a 5.5 mm diameter nozzle can create pressures of 6,000 psi) to create a long, thin continuous barrier. If the nozzle is rotated, a three to seven foot diameter cylinder can be formed (USEPA, 1998; USEPA, ITRC and RTDF, 1999). A wall of about 75% iron mixed with soil can be created. Because the equipment is small in size, installation cost are generally low. Pilot tests by DuPont are analyzing the feasibility of using guar gum as an ingredient in a 50 mesh iron particle slurry (USEPA, 1998).

Well bores are drilled to the bottom depth of the barrier. The nozzles are lowered to the bottom. A high pressure, high flow of reactive slurry is sprayed out as the nozzle is raised. The flow can be stopped before the ground surface is reached if the barrier does not need to be placed that shallow. This is an additional advantage over conventional trenching. Multiple borings can be placed at the proper distances so that media coalesce into a continuous barrier (USEPA, ITRC, and RTDF, 1999).

Jetting of soilcrete (grouted soil) columns can be utilized for impermeable wall installation, i.e. the funnel portion. Bentonite is injected through the nozzle of a drill bit system. The nozzle is lowered to the deepest portion of the wall, and materials are sprayed out as it is raised up. Fine soils are forced out of the reactive area and up to the ground surface. A 50% soil and 50% bentonite column is typically formed. If the subsurface largely consists of fine soils, then a more bentonite rich column is created as the fine particles are sprayed up to the ground surface (Gavaskar *et al.*, 1998).

Jetting has been used for barrier emplacement on active sites. The small equipment can fit around site obstructions. The nozzles can be positioned to jet around subsurface utilities so that their activities are not compromised (USEPA, ITRC, and RTDF, 1999).

Soilcrete columns can also be installed using deep soil mixing. Augers in series with mixing paddles suspended by a crane are driven by a motor. A bentonite slurry is injected through a drill stem as the augers move upward in order to create 40-60% grout columns. Depths of 120 feet can be reached with little spoils created, but the large equipment needed is expensive to operate (Gavaskar *et al.*, 1998; USEPA, 1998).

2.2.6 Fracturing

As with jetting, fracturing can be used when only a few inch thickness of Fe is required. Because the iron is the greatest part of the PRB's cost, practices that avoid excessive iron should be used (USEPA, ITRC and RTDF, 1999).

For media emplacement in rocky soils, vertical hydraulic fracturing can be used to create fractures to house media and conduct water. Holes are bored to initiate the fractures as a slurry gel of biodegradable materials is added under a high pressure, low velocity regime (Wickramanayake and Hinchee, 1998; USEPA, 1998; USEPA, ITRC, and RTDF, 1999). This gel is formed from cross-linked hydroxypropylguar, which is used as a thickener in the food industry. It is insoluble and viscous enough to hold iron filings in suspension when cross-linked. An enzyme is added that breaks the linkages so that only water and sugar remain. Therefore, little residue is present to interfere with the iron's activity. A three to four inch thick iron wall remains. Injections can be made into multiple wells so that continuous coalesced fractures are created. This technique has advantages over trenching and shoring in that it creates minimal site disturbance, generates minimal wastes, doesn't disturb groundwater flow, is low cost, and can be used to treat deep plumes (Wickramanayake and Hinchee, 1998).

Quality assurance can be achieved through the use of electrical resistivity. Salt is added to the slurry so that it is more conductive than the subsurface. A current is applied to the area of interest. A PVC pipe wrapped in a copper wire is inserted to pick up the signal. The locations the signals travel to indicate where the slurry has moved. These electrical signals can be coupled with computer software so that the spread of the reactive zone can be observed visually in real-time. This allows personnel to turn off the nozzles once two adjacent injection plumes have reached each other. In this manner, a continuous wall can be created with no excess use of media (USEPA, ITRC, and RTDF, 1999).

Bedrock must also be treated if it has fractures in it that allow for contaminated groundwater to flow under an installed PRB. Reactant sand fracturing is a high pressure technique that uses a sand proppent to inject low density iron particles into bedrock fractures (Marcus, 1999; USEPA, 1998). Proppents are ceramic beads coated with the reactive material (USEPA, ITRC and RTDF, 1999). The sand proppent must be used in a fracturing fluid, as iron does not possess suitable hydraulic properties (USEPA, 1998). It must be able to withstand pressures of up to 3,000 psi and pumping rates of 1,000 gallons per minute (gpm) without losing reactivity. The high pressure proppent injection results in increased hydraulic conductivity so that contaminated water can flow through and be treated by ZVI foam (Wickramanayake and Hinchee, 1998).

This technique was field tested in a former leachfield from a plating shop. Cr and chlorinated solvent contamination was moving in a 60-foot-wide plume through weathered volcanic bedrock 30 to 40 feet deep at a velocity about 7% of that of the groundwater. Both a zinc-alloy coated aluminosilicate and Cercona ZVI foam were tested with the latter having a greater reactivity and longer life. Three hundred to seventeen hundred pounds of 1 mm diameter proppents suspended in a fracking fluid with a polysaccharide viscosifier were applied to each zone. Guar gum breakdown products and fine sediments were removed so that permeability and reactivity were

not affected. Bromide tracer tests revealed that the fluids moved a minimum of 42 feet from each injection point and that hydraulic conductivity in the bedrock increased by two orders of magnitude. Concentrations of dissolved zinc and iron were found to increase above background levels but remained below toxic levels of concern (Wickramanayake and Hinchee, 1998). Fracturing has also been used to remediate a TCE plume at the Caldwell Trucking Superfund Site in New Jersey (USEPA, ITRC, RTDF, 1999).

2.2.7 Blasted Bedrock Zone

Contaminated groundwater in bedrock can be remediated by the blasted bedrock zone trench technique, also known as the refractive flow and treatment concept. A hydraulic conductivity contrast is created and manipulated to refract contaminant flow lines toward the reactive media. Regular funnel and gate systems differ as they rely on reflection, rather than refraction, to direct hydraulic paths. That is, the refractive technology alters the direction of the plume's flow by providing a path of least resistance through the subsurface. By contrast, in a funnel and gate system the impermeable walls direct the plume towards the gate similarly to the way a mirror reflects light. A plume moving toward the funnel is forced to change direction by "bouncing off" of it. Precision blasting is incorporated in the contaminated region to connect zones of permeability and upstream of the plume to divert clean water around it. Installation costs range from \$120 to \$200 per lineal foot (IBC, 1999).

2.3 Monitoring, Maintenance, and Longevity

Because of the short history of the PRB technology and the site specific nature of the application, only suggestions on monitoring techniques and frequency can be made. Specific plans must be dependent upon the site's unique contamination problem, hydrology, geology, and chemistry. Five factors should be considered when developing a monitoring program: 1) regulatory issues, 2) mechanism of remediation, 3) distribution of contaminants, 4) available groundwater sampling methods/equipment and 5) design of the barrier (Warner *et al.*, 1998). For example, the effluent from a funnel and gate covers a smaller area than that from a continuous barrier, so that monitoring wells will not be spread out over a wide area and can be clustered closer together to obtain a denser monitoring pattern (USEPA, ITRC, and RTDF, 1999).

Monitoring can be performed to achieve two goals: regulatory compliance and performance verification. Compliance monitoring is required and determines whether clean up goals are being met on the down-gradient side of the barrier. Conversely, performance monitoring is voluntary and focuses on the wall itself not on the site boundaries or compliance points. It is utilized for research purposes and as an early warning sign to decreases in barrier performance (USEPA, ITRC and RTDF, 1999).

Monitoring constitutes the major operating costs for the structure's lifetime. Therefore, activities should be made as efficient as possible by the proper positioning of wells and by the measurement of parameters that will give the most information about the subsurface conditions (Gavaskar *et al.*, 1998). Many of the subsurface properties analyzed in the site characterization phase are those that should be measured to assess barrier performance. Parameters, such as pH,

E_H , dissolved O_2 , Fe^{2+} , S^{2-} , and alkalinity, are inexpensive to determine and provide much information about subsurface activities (USEPA, ITRC, and RTDF, 1999).

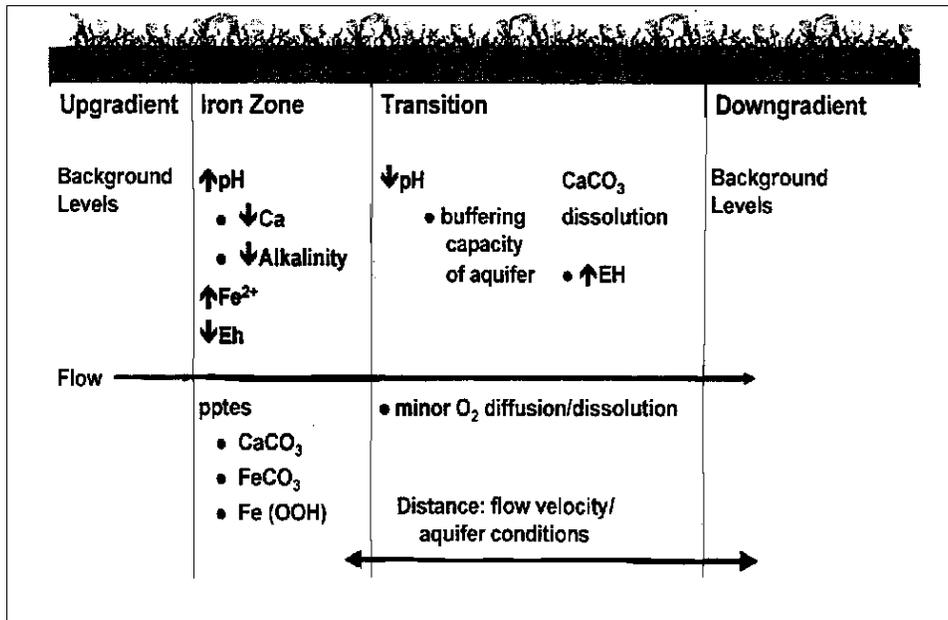


Figure 12. Chemical Changes Occurring due to ZVI Activity. Monitoring for these constituents can provide important data about the barrier's performance (USEPA, ITRC, and RTDF, 1999).

Hydraulic conductivity must be continually analyzed down-gradient of the reactive area to determine if plugging is occurring. This is especially necessary with inorganic contaminant remediation, as removal is achieved by sorption or solid precipitation, unlike treatment of organics, where the molecules are degraded. Because monitoring of water quality is required for compliance, chemical conditions and contaminant concentrations must be analyzed down-gradient from the media in order to determine whether leaching of sorbed species or toxic degradation products is occurring. Sorption/desorption events are especially susceptible to changes in pH. Therefore, this parameter must be continually analyzed (ITRC, 1998).

Design parameters should have been thoroughly considered so that the entire plume is captured and the media is thick enough to provide the proper residence time for contaminant removal. To be certain that these parameters were calculated correctly, contaminant breakthrough from the media and escape under, over or around the barrier must be ascertained by the proper positioning of monitoring wells. Breakthrough monitoring should be performed from wells placed directly in the media and not in any surrounding pea gravel, which may have stagnant water that is not representative of the entire reactive area. Clustered wells positioned at various depths in PVC piping can be used to detect vertical heterogeneity within the media (Gavaskar *et al.*, 1998).

Down-gradient water quality can be ascertained by measuring pH, E_H , and other parameters with long screen wells. These wells can take samples all along a vertical axis except for the top and bottom inch. These down-gradient measurements must be taken to determine if water quality parameters have rebounded after being altered by the media conditions (Gavaskar *et al.*, 1998).

Funnel and gate systems can be built with sampling wells permanently installed in the media. A group of wells can be suspended with a metal framework before the area is back filled. The frame can then be removed and reused after the media is in place. There are no regulations on the rate at which groundwater must be extracted from the subsurface for analysis. It is recommended that sampling in the media be performed with a slow, small purge so that hydraulic flow and contaminant residence time is not disrupted by well pressure (ITRC, 1998). To produce this passive sampling technique, wells should be of a small diameter (1-2 inches) and operated at a purge rate of 100-500 mL/minute. (USEPA, ITRC and RTDF, 1999). Besides changing residence time, a fast purge can cause an unrepresentative sample to be extracted. Micropurging should be utilized in order to reduce the chances of collecting untreated water from the up- or down-gradient side of the wall (Warner *et al.*, 1998). So that an artificial gradient is not created, a series of wells which are purged at identical rates can be installed along a flow path. A difference in subsurface conditions between two wells along the same path can give an indication of reactor performance (Gavaskar *et al.*, 1998).

Wells can also be positioned on the outsides of funnels. It is assumed that no water moves through these structures. But if there is doubt, samples can be taken to assure that none of the plume is escaping (Gavaskar *et al.*, 1998).

Early monitoring results may be unusual, as disruption to soils that occurs during installation can alter groundwater constituents (ITRC, 1998). In order to keep costs low, sufficient time for the plume to actually reach the PRB should be given before much monitoring occurs. Aging of the media and lifetime estimates can be determined by an analysis of time-scale changes in subsurface properties and from an examination of media core samples (Gavaskar *et al.*, 1998). Cores taken from the ZVI barrier in Elizabeth City, North Carolina, have revealed that iron corrosion coatings are present only on the first few inches of the up-gradient side of the wall (USEPA, ITRC, and RTDF, 1999).

Long-term performance evaluations of various walls are being led by Robert Puls, Nic Korte, and Charles Reeter at USEPA, DOE, and DOD sites, respectively (RTDF, 1999b). The DOE research consists of evaluations of potential cost savings for long-term monitoring. Micro-sensor monitoring methods are being considered (RTDF, 1998). Puls's research team at the Subsurface Protection and Remediation Division of the EPA's National Risk Management Research Laboratory is conducting studies to elucidate the longevity and aging process of PRBs. Team members are performing chemical and microbiological analyses on Fe cores from five to seven sites in order to accomplish the following objectives:

- Characterize the type and nature of precipitate formations;
- Determine microbial activity in response to Fe walls; and
- Develop long term monitoring and maintenance protocols that minimize operating and management costs and that can provide early warning signals to performance losses (RTDF, 1998).

Industry researchers are also evaluating long-term performance of barriers. Those from EnviorMetals have taken iron cores from two pilot scale installations: a Colorado Air Force base

and a New York industrial facility. Results indicated that carbonate precipitates were responsible for 6-10% losses in porosity and that biofouling was not a problem (Vogan *et al.*, 1998).

Additionally, methods to rejuvenate exhausted materials are being researched. Ultrasound vibrations are being considered when reduced permeability (plugging) is the problem. Acid can also be applied to remove carbonate precipitate build up, with oxalic acid showing the most promise. However, acid introduction presents regulatory problems and has the potential to cause corrosion of the Fe materials (USEPA, ITRC, and RTDF, 1999).

Some estimates predict that maintenance will be necessary every five years in highly mineralized aquifers and between 10 and 15 years for groundwater with a low mineral content. However, this is highly variable and very site specific. It can vary according to flow rates, contaminant type and concentration, pH, biological or chemical fouling, E_H , media and soil particle size, colloidal loss, and many other factors (ITRC, 1998).

Maintenance can be made easier if a removable cartridge system is used within the barrier gates. They facilitate the rapid replacement/regeneration of exhausted media (Subsurface Contamination Focus Area, 1999). However, as will be illustrated in the Y-12 site case study, the system must be properly designed so that maintenance is possible without the use of heavy machinery that can be very costly to use. A site in Portsmouth, Ohio, is treating organic contaminants with 55-gallon drums of ZVI in an above ground building. The building is at a low elevation so that gravity passively moves the plume through the media. This configuration allows the media to be changed easily. However, work at this site has indicated that ZVI may not be an ideal media choice, as plugging is frequently occurring (Phillips, 1999).

2.4 Closure

Closure protocols and regulations are undefined at this point because the PRB technology has no historical perspective. It is a new technology that has not yet seen a wall surpass its prime (ITRC, 1998). Because a closure has not yet occurred, important factors to consider can only be assumed. If the media is excavated or partially replaced, it may have to be disposed of as a hazardous waste. Unlike organic contaminants that are degraded to innocuous products, inorganics remain sorbed to the barrier or in the reactive area as a precipitate. Media treating radionuclides must be handled and disposed of especially carefully, according to radioactivity guidelines (ITRC, 1998).

Because metal and radionuclide solids are concentrated within the reactive area, there is speculation that resource recovery may be possible during maintenance or closure events. However, due to the short history of PRBs and their limited use for treating inorganics, the opportunity has not been encountered. Laboratory research, to date, has not addressed this issue (USEPA, ITRC, and RTDF, 1999).

The opportunity for resource recovery and the ultimate fate of the subsurface upon remediation is very site specific. Recovery of metals would only be economical if a great enough concentration is reached before contaminant breakthrough or exhaustion of the media occurs. If sorbed species

or solid precipitates are diluted in the media, then the whole mass will have to be disposed of as a hazardous waste upon site closure or during barrier rejuvenation events. For organic-based sulfate-reducing PRB systems, the media and transformed contaminants may be left in the ground if the subsurface can maintain naturally occurring reducing conditions once media reactivity is lost. However, if the EH rises naturally after the barrier is exhausted or if site disturbances that introduce oxygen to the reactive area are likely to occur, then the media and transformed contaminants must be removed upon closure. Otherwise, the pollutants may have the potential to become remobilized and to recontaminate groundwater. Once again, this is all very site specific (Ludwig, 1999).

3 Specific Examples

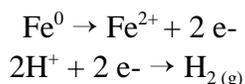
3.1 Inorganic Contaminant Information

Some of the inorganic contaminants treated by PRBs are described below. The properties and behaviors that can be manipulated to remediate groundwater contaminated with these pollutants are discussed. Remediation of groundwater contaminated with inorganic pollutants is achieved by making them less mobile or by lowering their bioavailability. Reducing their water solubility achieves these two goals. Remediation is not accomplished through destruction of the pollutants, as can be done with organic pollutants.

3.1.1 Arsenic

Arsenic exists in three common oxidation states: 3+, 5+, and 0. As(III) is the most toxic and mobile, but As(V) is also mobile. Laboratory research has been aimed at using ZVI to reduce As in the +3 or +5 state all the way down to As⁰, which is a solid. This, however, needs more testing before it can be applied in the field (USEPA, 1998).

ZVI has been found to remove greater than 95% of the As present in both laboratory and field tests conducted at the University of Connecticut, but by surface precipitation, not a redox reaction. As(V) removal was found to be greater than that for As(III) because it exists as an oxyanion while the latter is neutral. Arsenite (+3 valence) predominantly exists in a neutral oxide in natural waters: H₃AsO₃⁰, as the pK_{a1} is 9.20. Arsenate (V) predominantly exists in one of two anionic forms: H₂AsO₄⁻ and HAsO₄²⁻, as the pK_as are 2.91 and 6.94. Arsenate binds tightly to the Fe filings, so that removal efficiency was related to the Fe's surface area, which can increase over time due to ferrous oxide dissolution and addition of sand coatings. The ZVI is oxidized to ferrous iron as hydrogen ions are reduced to hydrogen gas by the following reaction:



This results in a positively charged iron surface which sorbs the arsenate species by electrostatic interactions. An increase in pH occurs as hydrogen ions are consumed (Lackovic, Nikolaidis and Dobbs, 1999).

Sulfate introduction into test columns was also analyzed. If the sulfate (SO_4^{2-}) is reduced to sulfide (S^{2-}), then an AsS solid can form. However if reduction does not occur, SO_4^{2-} anions can compete w/ the arsenite species for sorption sites on the ferrous iron. As also exists in sulfide complexes with Fe, Ni, and Co (Lackovic, Nikolaidis and Dobbs, 1999).

3.1.2 Uranium

It was not initially clear whether the mechanism of uranium removal from contaminated water is by a reductive precipitation or by sorption to an iron corrosion product. Research indicates both may be occurring, sorption to ferric oxide and reduction from ZVI's oxidation (NATO, 1998). ZVI has long been used to precipitate vanadium (V) from mining leach solution, and many natural ore deposits occur from the reduction of uranyl to uraninite (RTDF, 1998).

In laboratory tests, uranium removal by ferric oxides reaches equilibrium in less than one minute. However, more than 80% of the uranium remains in solution. This indicates that sorption is acting as the removal mechanism, as sorption equilibrium is reached quickly, but the surface sites rapidly become saturated so that no more uranium can sorb. Equilibrium with ZVI takes longer. But none of the uranium remains in solution after one hour. This is indicative of redox reactions acting as the dominant removal mechanism. U(VI) is reduced to U(IV), which exists as an oxyhydroxide solid or a precipitate on the ZVI surfaces. To further determine which oxidation state the uranium is in after interacting with ZVI, a CO_3^{2-} solution was introduced. It would have the ability to wash out the uranium if it were in the +6 oxidation state. The solid $\text{UO}_2(\text{CO}_3)_2^{2-}$ would form and be repelled from the negative Fe surfaces. Only a small fraction of the uranium could be washed out. This indicates that most was reduced by the ZVI to U(IV) and, hence, could not form the carbonate solid (NATO, 1998):



Because the reduction potential for UO_2^{2+} 's reduction half-reaction is greater than that for Fe, it is thermodynamically favorable for the U(VI) to become reduced. The Fe half reaction will run in reverse so that the Fe^0 will be oxidized. The E_{H} value will then be +0.44V. The Fe reaction is written above in the opposite direction from the way it will proceed in a PRB because it is convention to always write a half reaction as a reduction. A redox reaction is more favorable if it has a greater difference between the E_{H} values for each of its half reactions. This reaction will have a difference of 0.36 V (-0.07 - -0.44). However, the two E_{H} values should be compared at identical pH values. The E_{H} value for the uranium half-reaction will not be same at a neutral pH (7) as it is at 8. It is expected to be higher because more protons will be present as the pH is lowered. The addition of more reactants (protons), will cause the reaction to proceed further to the right. This should result in a greater difference between the two half reactions' E_{H} values and, hence, a more favorable reaction.

The removal efficiencies of Cercona Fe bone char, Wards peat, and ferric oxide were compared over a range of uranium concentrations. The Fe bone char was found to be most effective at low U concentrations. However, peat was two to three times more effective than the Fe bone char and

five to six times more effective than ferric oxide at high uranium concentrations (NATO, 1998). Additionally, phosphates can form a solid precipitate (UPO₄) with uranium.

3.1.3 Chromium

Cr(VI) is highly toxic, carcinogenic, and extremely mobile (USEPA, ITRC, and RTDF, 1999). Its reduced form, Cr(III), can exist either as a precipitate surface in a hematite structure as Cr₂O₃ or as an iron-containing solid having a goethite structure (Fe_(x-1)Cr_(x)OOH). A chromium hydroxide solid can also form (USEPA, 1998). Chromium reduction by ZVI oxidation is favorable as the half reaction under standard conditions for Cr(VI) reduction to Cr(III) is as follows:



(Artiole and Fuller, 1979; Snoeyink and Jenkins, 1980). Figure 13 illustrates the reduction of Cr⁶⁺ (CrO₄²⁻) to Cr³⁺ by ZVI and the resulting precipitation of hydroxide solids.

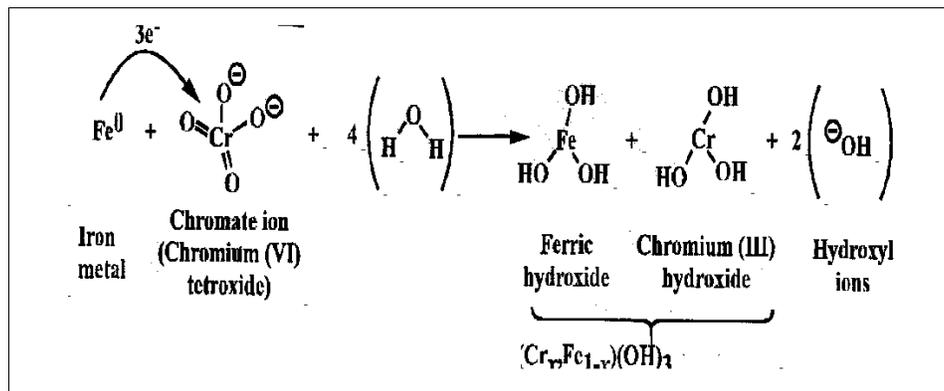


Figure 13. Cr Reduction, Fe Oxidation, and the Subsequent Solid Formation (USEPA, 1997).

3.1.4 Nitrate

ZVI has been laboratory tested for NO₃⁻ removal. However, in an abiotic setting, NO₃⁻-N was reduced all the way to NH₄⁺-N, which is also an undesirable form of N. To promote biological denitrification reactions, which convert NO₃⁻ to N₂ gas, a carbon source can be added to the anoxic subsurface (USEPA, 1998). Denitrifiers are anaerobic micro-organisms that use NO₃⁻ as their TEA. They ultimately reduce it all the way down to N₂, which is the gas that comprises 78% of the Earth's atmosphere. Nitrogen is unique in that it can exist in several different oxidation states. Starting from the most oxidized, common states are as follows:

Name	Molecular Formula	Oxidation state
Nitrate	NO ₃ ⁻	+5
Nitrite	NO ₂ ⁻	+3
Nitric Oxide	NO	+2
Nitrous Oxide	N ₂ O	+1
Nitrogen gas	N ₂	0

The World Health Organization has set limits on NO_3^- -N at 10 mg/L. Ammonia/ammonium exhibit acid-base behavior with the pKa value, the pH at which half of the molecules exist as NH_3^+ and half exist as NH_4 , being 9.3. Ammonium is a noxious gas that is very irritating to the nasal tissues.

Nitrite (NO_2^-) in drinking water has been associated with methaemoglobinemia (blue baby syndrome). Therefore, media treating nitrogenous contamination must be properly sized to deal with this toxic transformation product.

3.1.5 Mercury

Hg removal has not been extensively studied. The Kerr Research Laboratory has performed some preliminary analysis of mercury and ZVI interactions to the conclusion that mercury is removed from the aqueous phase. However, the mechanism of removal has not yet been elucidated (USEPA, ITRC and RTDF, 1999). Because mercury in the zero valence state exists as a gas, the potential for reduction to a mobile gas exists and should be considered, as a reduction in mobility is the major goal of metal remediation.

3.1.6 Others

Strontium (Sr^{2+}) can sorb on minerals and on amorphous Fe coatings by cation exchange (Wickramanayake and Hincee, 1998). Technetium (Tc) and selenium (Se^{6+}) reduction by Fe to solids have also been seen in the laboratory (USEPA, 1998).

Recovery of metals would only be economical if a great enough concentration is reached before contaminant breakthrough or exhaustion of the media occurs. If sorbed species or solid precipitates are dilutely mixed in the media, then the whole mass will have to be disposed of as a hazardous waste upon site closure or during barrier rejuvenation events. For organic-based sulfate-reducing PRB systems, the media and transformed contaminants may be left in the ground if the subsurface can maintain naturally occurring reducing conditions once media reactivity is lost. However, if the E_H rises naturally after the barrier is exhausted or if site disturbances that introduce oxygen to the reactive area are likely to occur, then the media and transformed contaminants must be removed upon closure. Otherwise, the pollutants may have the potential to become remobilized and to recontaminate groundwater. Once again, this is all very site specific (Ludwig, 1999).

3.2 Case Studies

Following are case studies of four sites using PRBs to treat inorganic contamination. Also included are outlines of sites that have been documented in other sources. The Oak Ridge, TN site has previously been documented in the literature. However, a short case study is included here to provide some “lessons learned” information that may not be documented in any other sources.

3.2.1 Y-12 Site, Oak Ridge, Tennessee

The Bear Creek, in the ten mile long, east/west running Bear Creek Valley is threatened (RTDF, 1998) by four distinct groundwater plumes that are spreading U, Tc, and NO_3^- contamination from the Y-12 pond. Two of these plumes have undergone remedial activities, while the two others remain unremediated (Phillips, 1999). Liquid wastes were added to disposal ponds from 1952 to 1981 (USEPA, 1999), with over 2.5 million gallons being disposed of each year (RTDF, 1998). The site was capped in 1983, but leaching from the ponds has contaminated both surface and groundwater (USEPA, 1999).

The 400 ft² x 17' deep pond (RTDF, 1998) overlies karst geology (Phillips, 1999). The unconsolidated clay underlying the site has a low permeability of 4×10^{-7} inches/sec, while the weathered bedrock has a greater permeability of 4×10^{-4} inches/sec. The saturated zone is 10 to 20 feet thick and begins 10 to 15 feet below the ground surface (USEPA, 1999).

Pilot scale studies were conducted to compare the effectiveness of ZVI filings, peat materials, ferric oxides, and Cercona Bone-Char. ZVI was found to be more effective for removing U than the absorbent materials, especially at high uranium concentrations. A combination of peat and ZVI was determined to be efficient for removing mixed plumes of U and NO_3^- . It was noted that the U^{6+} was reduced to a U^{4+} solid by ZVI and coprecipitated, but not reduced, by ferric oxyhydroxides. This was determined by the fact that the introduction of O_2 resulted in a remobilization from the former media, but not from the latter (NATO, 1998).

The remedial costs for both walls was approximately \$1,000,000, which includes design, construction, materials, and media (USEPA, 1999).

Pathway 1: In December 1997, a 220-ft system consisting of two wing walls oriented to channel groundwater into a vault containing treatment canisters was installed. The emplacement was only twenty five feet deep, but it was expected that the natural groundwater gradient and the permeability contrast between the gravel backfill and the native materials would induce plume flow (USEPA, 1999). However, the groundwater flow into the reactive area proved to be insufficient for passive remediation to occur. The HDPE wings designed to funnel water to the piping in the vault actually caused upwellings on the upgradient side. Consequently the system had to be pumped. The system was redesigned with a pit downgradient of the vault in order to initiate better groundwater flow (Phillips, 1999).

The vault contained a framework of six 55-gallon canisters containing peat moss, ZVI, and various combinations of these materials. They were designed in a shallow vault (twenty-five feet deep on palettes) so that replacement of exhausted media could be achieved easily. However, a large crane was required to lift the vault door and frame for any work to be performed on the system. This heavy equipment is very expensive, costing thousands of dollars a day to use. Additionally, it was found that rain water leaked into the vault through the door (Phillips, 1999).

Chemical problems, such as clogging of the iron, were also encountered. The effluent's level of Fe^{2+} went up over time, reaching 150 ppm. It is not known whether biological activity, which

was encouraged by the guar gum used to install the trench, was the cause of this problem. The system was effective at removing U and Tc from the groundwater. But the plugging, leaking, and need for pumping were problematic enough that the system is currently not operating (Phillips, 1999).

Pathway 2: In November 1997 a 225 x 2-ft thick by 22 to 30-ft deep continuous trench was installed. Gravel filled all but a twenty-six foot stretch in the middle, which contained eighty tons of ZVI. The trench was positioned parallel to the direction of groundwater flow and perpendicular to the plume's direction of flow (figure 14) and was installed with a guar gum (USEPA, 1999).

Concentrations of uranium decreased over time within the reactive area. pH levels rose to greater than 9 in the iron filings, but dropped to ambient levels about 50-ft down gradient. Tc and NO_3^- contamination was also removed by the barrier. Additionally, Ca, $\text{CO}_3^{2-}/\text{HCO}_3^-$ and SO_4^{2-} concentrations were found to have decreased. SO_4^{2-} losses could have been from SRB activity, as the iron barrier created reducing conditions for these micro-organisms. Additionally, plugging by Fe oxides, CaCO_3 , and FeS occurred (RTDF, 1998).

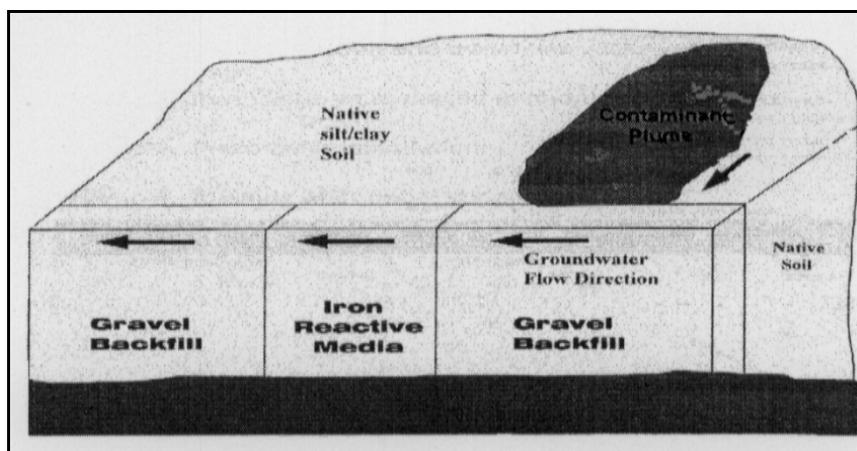


Figure 14. Conceptual Design of the Continuous Trench (RTDF, 1998).

A bromide tracer was used to assess flow paths along the wall. It was predicted that groundwater will actually flow across instead of down the wall during the wet season. Therefore, the wall will need to be longer and to discharge at a lower hydraulic head in order to operate passively through all seasonal events. It is planned that the barrier will be extended 100' further to the west (RTDF, 1998).

3.2.2 Coal Washery Alkaline Slag Leachate, Kemblawarra, Port Kembla, NSW, Australia

Site Background

Sand mining on the Garnock Engineering Property from 1976 to 1991 resulted in a fifteen meter deep pit. The area became filled with water and was eventually backfilled with three metric tons of industrial wastes from BHP Steelworks of Port Kembla. These wastes include air cooled blast furnace slag, steel making slag and coal washery discard.

The water table depth was such that the top 0.3 to 0.8 m of slag remain unsaturated during normal conditions. However, the August, 1998 rainfall in the Woolongong area was recorded to be 602.5 mm, which was 5.5 times greater than the mean area rainfall for that month (88 mm). This caused the water table in the fill area to rise up to the ground surface at the end of August.

In September 1998 a groundwater outflow was noted in a previously existing SE-NW angled depression known at the Tank Trap. It was leaving the property via a double pipe culvert in the Tank Trap. This outflow discharged further west into Lake Illawarra via the canal. Ecotoxicological impacts were observed from the influx of this highly alkaline, HS⁻ rich water.

Initial Actions

The Lake Illawarra Authority installed a boom and curtain in Griffins Bay in order to block this influx. Influx monitoring indicated that the contamination originated from slag leachate.

Blast furnace and steel making slag are classified as inert wastes and are, hence, exempt from any landfilling guidelines established by the 1998 Solid Waste Management Regulations. However, since the mid-1980's it has been understood that slag emplacements have the capacity to generate high alkalinity leachates for long periods of time. These leachates also contain toxicologically relevant concentrations of HS⁻.

Site Characterization

Fill inspection revealed that the majority of the furnace slag is nominal 40 mm Crusher Run. The major mineral component of furnace slag is a member of the calcium aluminosilicate mellilite family [(Ca,Na)₂(Mg,Fe²⁺, Al, Si)₃O₇]. Mellilites comprise about 65% of the slag by volume. An interstitial iron-rich isotropic glass enclosing small oxide and sulfide crystals comprises about 20% by volume. Sulfur, which comprises about 2% by volume, exists in the glass crystals as CaS and MgS.

Data from laboratory studies of slag leachate (produced by saturating slag with fresh water) indicates the following properties:

pH	12.4-12.9
pe (-log [electron])	-10--9 (-590--530 mV)
Ca	360-720 mg/L
Mg	0.1-1.0 mg/L
Na	150-200 mg/L
K	30-70 mg/L
total alkalinity	1050-2100 mg/L as CaCO ₃
Cl	150-300 mg/L
SO ₄ ²⁻	3-300 mg/L (depending upon oxidation of the slag)
S ²⁻ /HS ⁻	1-200 mg/L (depending upon goethite on the slag and oxidation)
F	0.5-5.0 mg/L

Si	2-4 mg/L
Fe	<0.05 mg/L

Greater concentrations of Cl and SO_4^{2-} may occur if a saline groundwater is present, as in some Kemblawarra aquifers. SRB activity is not expected as there is no carbon source and survival above pH 9.0 is not likely.

On September 29, 1998, water samples were taken by EAST Laboratories of Port Kembla at the inflow to the Tank Trap pond, in the pond just upstream of the culvert and at the point of discharge to Griffins Bay in Lake Illawarra. pH levels of 12.2, 12.1, and 12.1, respectively, were measured. Sulfide concentrations of 3.71, 2.98, and 0.58 mg/L, respectively, were detected. The greatly reduced S^{2-} concentration in the bay than in the pond can be attributed to oxidation to SO_4^{2-} upon exposure to O_2 in the culvert. However, this lower level is still of toxicological concern. Throughout October, site investigations including pH measurements, dye tests and investigation trenches were conducted to determine whether:

- the granulated blast furnace slag grinding and washing plant in the South Coast Equipment site adjacent to the Garnock Engineering property could be totally or partially responsible for the alkaline groundwater outflow, or
- the Garnock Fabrication Building has any blast furnace slag in its foundation

Neither of these possibilities was supported by the investigations and were, consequently, disregarded. Following the substantiated hypothesis that all of the outflow was due to the backfilled sand pit, a network of shallow (0.5 m below the water table) 50 mm diameter, 2-3 m piezometers of PVC tubing open at the bottom was installed to the east and south of the Fabrication Building. This allowed for the elucidation of the depth of the compacted coal water discharge cover material and of the extent of the slag fill area around the building and Tank Trap pond.

pH measurements revealed levels as high as 12.7. Water table levels dropped from the time of initial measurements from the network on October 29, 1998. As of January 14, 1999, they were around mean elevations that had been determined in 1997 for the area. Outflow level observations indicate that outflow rates fluctuate quickly corresponding to rain water infiltrating the slag fill area.

Remedial Plan Development

Engineering solutions considered for the remediation included:

- Spray irrigate area with dilute sulfuric acid (H_2SO_4) to neutralize the alkaline leachate and to fully saturate the interstitial spaces between the slag pieces beneath the water table with gypsum. Gypsum precipitation would provide for a closure of the problematic volume and a self sealing of the slag surfaces. This would reduce the water flow through the slag and the production of leachate. This option was attractive in that it would provide a long term solution. But it would require an uncertain duration and cost due to the large volume of acid

needed and the long pumping times required to saturate the entire area. Additionally, treatment could only be ceased once a neutralization of the outflow was observed. Following this, it is possible that the gypsum would leach away over time, thus allowing alkaline leachate to again be generated. Slag fill on the South Coast Equipment land to north (which could not be treated in this way as it is not owned by Garnock Engineering) could bring more leachate onto the Garnock property. Lastly, there are health and safety issues involved with the handling, storing, diluting, and spraying of H_2SO_4 . Therefore, this option was not considered further.

- Install a cement grout or bentonite impermeable wall across and on either side of the Tank Trap to block outflow through the culvert. Due to the wet sandy soils, trench cutting is only feasible down to 0.5 m below the water table, which may not be deep enough to block the flow. Additionally, extensive hydraulic modeling would be necessary to determine how long the wall would need to extend beyond the Tank Trap to protect against overflow from heavy rainfall events. Lastly, costs of the trenching equipment operation and the wall materials would be costly. Therefore, this option was disregarded.
- Install a H_2SO_4 dosing plant with a compound return loop controller coupled to a outflow rate sensor at the point of leachate outflow from the Tank Trap. This would provide neutralization under all flow conditions. This option was also rejected because the costs of the equipment and the acid would be about \$30,000, overdosing and equipment failure could be problematic, and health and safety issues are connected to acid use.
- Install a permeable reactive wall in the Tank Trap east of the outflow point to passively neutralize the alkaline leachate. This option was chosen because it provides a green engineering solution which would not require extensive maintenance. However, this technology has never been used (to the knowledge of Egis Consulting Australia) to remediate alkaline leachate, so has no protocols or lessons learned that can be followed.

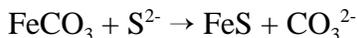
Treatment Wall Installation

In January, 1999, a 6000 ton coal washery discard PRB was installed near the outlet of the Tank Trap, about 4.0 meters east of the entry to the culverts. It was 1.0 m deep with a poured concrete pad base underneath. South Coast Coalfield coal washery discard has the following approximate composition:

quartz	25%
kaolinite	15%
illites	20%
calcite	2%
siderite	10%
combustibles (coal)	28%

The low silica leachate weathers the washery discard upon contact. This occurs rapidly by alkaline dissolution of fine grained quartz and mixed layer clays. Silica concentrations in the

leachate, consequently, increase substantially. Al, K, Mg, and Fe²⁺ concentrations also increase, to a lesser extent, in the leachate. Reductions in pH accompany these increases in dissolved constituents. Decreases in S²⁻ also result, by the following reaction with siderite (FeCO₃):



The FeS is a very insoluble solid, having a solubility constant (K_{so}) of 10^{-17.3} (Snoeyink and Jenkins, 1980).

The pond area of the Tank Trap was filled in with lightly compacted coal washery discard from South Bulli Mine, Bellambi and the coalwashery at Port Kembla Steelworks. These fillings (approximately 10,000 m³, 15,000 tonnes) were initiated directly behind the wall immediately following its emplacement. The pH of the water flow through the wall was extensively monitored.

Wall Performance

At the point of installation, when the washery discard fill behind the reactive wall was 5.0 m thick, the pH of the eluting water had dropped to 10.7 (from 12.6). The wall has been progressively widened to the east so that the pond has become completely filled. A thickness of 30.0 m has been achieved. Since the completion of construction, the pH of the water exiting the wall has equilibrated around 8.7-9.1. This is a reduction of more than 3.0 pH units. S²⁻ has been removed to < 0.01 mg/L.

The wall has only been *in situ* since January 1999. Plans are in place for Stuart Gray, PhD candidate in the Engineering Department at the University of Wollongong, to study leachate migration and the reactive wall's performance over the next three years for his dissertation research. The network of piezometers installed over the Garnock Engineering property will remain for the next three years to support his work. Additional piezometers have been installed on the downgradient side of the wall to continually monitor pH levels and S²⁻ concentrations.

A steel plate weir has been installed 4.0 m downgradient of the wall against the culvert head wall. It contains a high flow notch and a riser pipe primary outlet with a control valve. Flow rates and residence times can be controlled by using the weir to manipulate the hydraulic head difference across the wall. A cumulative water meter will be installed so that Gray can be supplied with groundwater flow rate data at various time points and averaged over various time periods.

Geochemical calculations have indicated that the reactive wall's ability to control alkalinity and S²⁻ should outlast the slag's ability to produce toxic leachate. The large volume of coal washery discard provides for a substantial residence time (> 3 days) in all weather conditions. As a final step in the remediation process, there are plans for a grass and shrub growing medium to be introduced over the filled Tank Trap pond. In this way, the site is aesthetically pleasing, remedial activities are unseen, and there is no human contact with hazardous substances.

References: except where otherwise noted, all information was provided by Short, 1999.

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3.2.3 Universal Forest Products, Incorporated, Granger, Indiana

Injections of calcium polysulfide and sodium bisulfite were utilized in this site's remediation strategy. The use of this technology does not result in a wall in the more conventional sense. Instead a reactive treatment zone is created. It is discussed with PRB technologies, as it is similar to them in that an *in situ*, passive remediation system is emplaced in the subsurface to reduce the mobility, bioavailability, and toxicity of the groundwater contaminants of interest, Cr(VI) in this instance. This is accomplished by altering chromium's redox state, which results in a change in its behavior and fate. At this site, initiation of the subsurface reactive zone is coupled with pump and treat, so that, overall, the remediation is not passive. However, the establishment of the reactive zone in the subsurface is accomplished passively via natural groundwater movement.

Site Background

In 1981, a wood treatment plant originally named Great Lakes Wood Preserving was opened at the southern end of the property at 50415 Herbert Street, Granger, IN 46530, by Universal Forest Products (UFP). The property is located in St. Joseph County, near the Michigan-Indiana border in the Judy Creek drainage basin, a tributary to the St. Joseph River.

Cr(VI), Cu, and As contamination affected groundwater as a result of spills and leaks of process solutions and the placement of snow containing wood preserving compounds onto unlined areas during the plant's early years of operation. In 1984, the plant yard was partially paved with asphalt. Surface runoff was collected in dry wells equipped with drainage grates bored into the vadose zone. In 1986, it became apparent that groundwater near and down gradient of the southern end of the property was contaminated with metals originating from wood treating chemicals.

Initial Remedial Efforts

Immediately after detecting Cr, Cu, and As contamination in 1986, UFP began pump and treat activities to reverse the groundwater gradient and remove metal contaminants. The southern plant was, subsequently, closed in 1987 as a more technologically advanced wood treatment plant was built at the northern end of the property. Pump and treat, with beneficial reuse of the water, continued and acted to prevent contaminated groundwater from exiting the site. These activities

were also successful in lowering off-site chromium concentrations. However, on-site chromium contamination persisted in the southern end's shallow saturated zone. UFP also drilled new, deeper wells for area residents.

Contamination Event from the Northern End Treatment Plant

Wells in the plume in the southern end supplied the water for the new treatment plant. Runoff from this new facility and the treated wood storage yard was channeled to a northeasterly located storm water holding pond. This pond was unlined, resulting in a groundwater contamination event in the northern end of the property.

In August 1993, monitoring wells were installed around the pond after it was suspected that the storm water contained wood treatment chemicals. Samples taken from these wells contained Cr concentrations just below the USEPA and Indiana Drinking Water Standards. There were no findings of off-site migration from the pond. At the same time, laboratory and field studies indicated that *in situ* immobilization of Cr could occur in the site's subsurface. Due to these results, UFP applied to the Indiana Department of Environmental Management's (IDEM) Voluntary Remediation Program on February 15, 1994.

In August and September 1994, four additional monitoring wells were installed around the detention pond. A portable down-hole submersible pump for purging and sampling was utilized to perform extensive monitoring well sampling. This resulted in the detection of another Cr plume in the northern area. It seems that this plume remained on-site.

South Area Remedial Action

Fluor Daniel GTI began site characterization efforts in August 1995. Throughout August and October, groundwater samples were taken from the pre-existing monitoring wells. They were analyzed for dissolved and total Cr(VI), dissolved and total Cr, dissolved and total Cu, and dissolved and total As and compared to background results from uncontaminated groundwater sources.

In September 1995, the remediation system, which is an integration of pump and treat and PRB technologies, was installed. Groundwater was pumped from recovery well RW-1 outside of the first wood treatment plant. Most of the groundwater extracted from RW-1 was used for wood treatment in the northern end building. The remainder of the water was used for the remediation process. A chemical metering pump introduced 29% calcium polysulfide into a pipe containing RW-1 water in order to reduce the Cr(VI) to Cr(III) through oxidation of the S^{2-} to elemental sulfur (S^0). The contaminants and amendments mixed and reacted in the pipes before they were discharged to a bag filter. The treated water was then reintroduced to the contaminated subsurface by a shallow horizontal infiltration pipework, where it diffused into blind interstitial voids. Redox reactions occur with the Cr(VI), which lightly interacts with the soil particles by electrostatic interactions, resulting in reduction to Cr(III), which forms immobile oxyhydroxide solids.

Initially the polysulfide reductant treated water was continually applied to the subsurface. But after a week of operation, continuous injection ceased, as it was observed that the rate of injection was greater than the rate of infiltration. Injections then occurred once a week on the following days in 1995: October 16, October 26, November 1, November 2, November 7, November 14, and November 21. In all, 197,999 gallons of groundwater were treated with 602 gallons of calcium polysulfide and returned to the subsurface.

The only equipment required for the treatment system was the following: turbine groundwater pump (RW-1), HDPE 6,500 gallon chemical storage tank, diaphragm chemical metering pump, filtration system, and subsurface infiltration gallery consisting of six perforated horizontal pipes three feet below ground level.

Monitoring of this area occurred weekly during operation of this remedial system (October 10, 1995 to November 28, 1995). Purging occurred until pH, conductivity, and temperature readings stabilized before each sample was extracted with either disposable polyethylene bailers or low flow purge pumps. The purge water from wells exceeding public health groundwater criterion and from those having Cr(VI) concentrations below these levels was discharged to the operating wood treatment facility and to the storm water retention pond, respectively. The pump and hose were cleaned before samples were taken by a rinse with Alconox solution and with distilled water.

Cr(VI) monitoring results indicated that only two wells exceeded the residential health-based groundwater criterion (0.10 mg/L). However, these concentrations dropped quickly once remediation began. Water from MW-6A dropped from 0.252 mg/L on October 31, 1995 to less than 0.005 mg/L on November 8, 1995. Similarly, samples from MW-6NE decreased from 0.459 mg/L to 0.048 mg/L on November 15, 1995.

Because monitoring indicated that *in-situ* Cr(VI) reduction/immobilization was occurring sufficiently to decrease concentrations below the residential drinking health-based criterion, remedial activity was stopped on November 21, 1995. Sampling on December 7 confirmed that this criterion was still being met. Confirmation sampling occurred on January 22, April 18, July 29, and October 23, 1996.

A surface spill of calcium polysulfide occurred when the hose connecting the chemical storage tank to the chemical feed pump broke. Clay pellets were used to absorb the spill. They were disposed of as non-hazardous waste in four fifty-five gallon drums and shipped to Waste Management Company's Westside disposal facility in Three Rivers, Michigan. No other wastes were created, excluding the purge water extracted from the monitoring wells in the plume.

Northern Area Remedial Action

Baseline measurements for dissolved and total Cr(VI), dissolved and total Cr, dissolved and total Cu, and dissolved and total As were taken in August and October, 1995 from monitoring wells in the area. Three units of sediments from the storm water retention pond were analyzed for Cr and As leaching potential. Sequential Batch Test leachings were conducted with air-sparged

deionized water. This is to predict whether rain water will leach contaminants out of the sediments after remediation has occurred. Results of this test indicate that sediment leaching will not pose a threat to groundwater sources.

In September and October, 1995, the remediation system consisting of two submersible groundwater pumps, a HDPE 6,500 gallon capacity chemical storage tank, and a diaphragm chemical metering pump was installed. Beginning on November 1, groundwater was pumped at a rate of 30 gallons/minute from each of 2 of the existing monitoring wells: MW-21 and MW-23, which are 120 feet south and 40 feet southeast, respectively, of the retention pond. The water was then treated with sodium bisulfite, which acts on Cr(VI) in the same fashion that the calcium polysulfide does, and discharged into the pond. Treated water from the pond percolated down to the water table and flowed back to the MW-21 and MW-23.

Purging and decontamination events were similar to those reported for the southern end remedial activities.

Weekly groundwater samples were taken from wells around the pond and analyzed for Cr(VI), SO_4^{2-} (occurs from oxidation of the bisulfite), and Na^{2+} , as operational monitoring was performed on the extraction wells and on the treated water before discharge into the pond.

Results of three operational monitoring samples are presented below:

	<u>November 8, 1995</u>	<u>December 28, 1995</u>	<u>January 3, 1996</u>
<u>MW-21</u>			
Na ²⁺ (mg/L)	6.68	17.5	14.1
SO ₄ ²⁻ (mg/L)	12	43	25
Cr(VI) (mg/L)	0.036	0.084	<0.005
<u>MW-23</u>			
Na ²⁺ (mg/L)	15.2	16.9	61.6
SO ₄ ²⁻ (mg/L)	15	45	89
Cr(VI) (mg/L)	0.058	0.082	<0.005

Remediation was ceased on December 28, 1995, when water extracted from MW-21 and MW-23 contained elevated Na²⁺ and SO₄²⁻. Concentrations of Cr(VI) had not decreased by this date, but the supply of sodium bisulfite had run out. It was decided that another sampling round would occur the following week (on January 3, 1996) before more reductant was ordered. At this time Cr(VI) levels had decreased. This indicated that the reducing treatment zone had migrated throughout the contaminated region, back to the pumping/monitoring wells, and it was decided that the remediation system would not be turned back on. During the period of November 1 to December 28, 1995, a total of 4,020 gallons of sodium bisulfite was used.

Pumping from MW-21 and MW-23 and discharge to the retention pond continued from December 28, 1995 to August 29, 1996 in order to move the sodium sulfite previously injected into the subsurface toward the wells. But extracted groundwater was not treated with the

reductant during this time. Quarterly monitoring was conducted on January 23, April 18, July 30, and October 23, 1996, to confirm the success of the remedial efforts and to assure no leaching of Cr from the sediments or reoxidation of Cr(III) to Cr(VI) had occurred. Results from these monitoring events, performed according to appropriate quality assurance guidelines, indicate that the residential health-based groundwater criterion for Cr(VI) has not been exceeded.

A remediation system in the central area of the property was initiated in January 1996. Sodium bisulfite treated groundwater was introduced to the subsurface through six injection points. MW-21 and MW-23 pumping during this time (without reductant added to the northern area) was used to analyze the effects injection from the six central area wells had on the water table.

Some problems were encountered during the operation of the northern end system. Between November 8 and 13, 1995, the aboveground hose carrying the reductant to the extracted groundwater froze. It was then buried about four feet below the ground surface to prevent this from occurring again. The chemical metering pump could not be operated on November 21, 1995, because the central area remediation system was being installed. MW-20, one of the monitoring wells utilized for the quarterly sampling could not be utilized on July 30, 1996, as the area surrounding the well was flooded.

Current Status of the Site

After a project duration of five years and two months, a certificate of completion has been issued, and the site was listed as completed according to Tier II Residential objectives on April 20, 1999. A Covenant Not To Sue had been submitted to the Governor's Office.

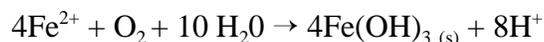
References: all information from Indiana Department of Environmental Management, 1999.

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3.2.4 Acid Mine Drainage, Vancouver, Canada

Site Background

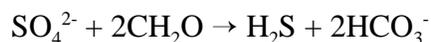
This industrial site in Western Canada has historically received sulfide mineral ore concentrates for shipment to foreign ports. Storage of these ores has resulted in acid drainage rich in Cu, Cd, Ni, Pb, and Zn that threatens a nearby marine ecosystem. When metal sulfides are exposed to air and water, acid is produced, increasing the solubility of the metals. In the case of ferrous Fe, the now-soluble metal can be further oxidized to produce more acid (H^+) by the following reaction:



The sand-gravel aquifer's hydraulic conductivity averages 10^{-2} - 10^{-3} cm/sec (0.5 ft/day). The net groundwater flow moves south toward a marine inlet.

Remedial Actions

Conventional pump and treat methods would have to be operated for decades to remediate the site to appropriate conditions. Costs to excavate and dispose of contaminated soils would have exceeded \$50 million. Following the success of the remedial efforts at the Nickel Rim site in Sudbury, a compost PRB was chosen. Results from this site and from laboratory studies indicate that leaf compost can act as a suitable source of carbon, nitrogen, phosphate and trace elements for SRBs. Compost also acts as an electron donor, with SO_4^{2-} acting as the TEA, in the following reaction:



The sulfides ($\text{S}^{2-}/\text{HS}^-$) produced complex with the dissolved metals to form very insoluble metal sulfide solids. The carbonate produced raises pH and buffers the system. Studies of site aquifer materials indicated that the hydraulic conductivity through the wall must exceed 0.03 cm/sec and that a media mixture containing 85% pea gravel could achieve a conductivity of 0.15 cm/sec.

In March 1997, a 10 m long by 2.5 m thick pilot scale test wall was installed to a depth of 6.7 m below grade in a region of high groundwater and soil contamination by cut and fill excavation methods. A backhoe was used to thoroughly mix the reactive media (80% pea gravel, 15% compost, 5% limestone) above ground prior to emplacement. A low viscosity guar gum slurry was utilized to support the trench before the media was filled in by a clamshell. The pea gravel maintains a high permeability through the barrier, and the limestone raises the pH, providing a suitable environment for the micro-organisms.

Materials costs were \$25/yd³ for pea gravel and \$52/yd³ for limestone; the compost was free from the city of Vancouver.

Sampling

Seventeen bundle-style multi-level piezometers were installed in the vicinity of and within the wall. Each monitoring bundle was comprised of seven sampling points spaced about 0.5 m apart, beginning just below the water table. The deepest point in each was below the wall to detect potential underflow. Six bundles were installed within the wall, and nine were outside in the plume's path (three upgradient, six downgradient). One bundle was installed on each side of the wall in order to detect plume by-pass. Beginning one month after installation, groundwater samples were collected once every three months. Contaminant concentrations were quantified in the laboratory, as pH, E_{H} , alkalinity, and sulfide measurements were conducted in the field. Sealed flow-through cell electrodes were used for the pH and E_{H} determinations. Sulfuric acid (H_2SO_4) titrations with a digital titrator were utilized to determine alkalinity. Sulfide measurements were performed with a spectrophotometer.

Results

The guar gum degraded within three to four weeks after emplacement. Piezometer measurements within the treatment wall indicated that the hydraulic conductivity averaged 0.18 cm/sec through the reactive zone. Vertical gradients, which are tidally influenced, were downwards between 5×10^{-5} and 1.5×10^{-4} . Conductivity through the media is sufficient to deter hydraulic head build-up and plume diversion.

Analysis of groundwater samples taken from the middle (laterally) of the plume (ML-2, ML-6, ML-10, ML-13) in June of 1998 (15 months after emplacement) reveals the following:

- E_H dropped from 452 mV upgradient of the wall to 6.5 at the backside of the wall and then rose back to 100 mV at the downgradient side.
- Alkalinity increased from 99 mg/L (as CaCO_3) on the upgradient side to 344 mg/L on the downgradient side.
- Sulfide increased from $<1.0 \mu\text{g/L}$ on the upgradient side to $1700 \mu\text{g/l}$ in the front side of the wall and then dropped to $130 \mu\text{g/l}$ on the downgradient side.
- Cd decreased from $23 \mu\text{g/l}$ on the upgradient side to $<0.1 \mu\text{g/l}$ at all other wells along the path.
- Cu decreased from $2.25 \mu\text{g/l}$ on the upgradient side to $1.9 \mu\text{g/l}$ on the back side of the wall. It then rose to $3.4 \mu\text{g/L}$ at the first downgradient well (ML-13).
- Ni decreased from $155 \mu\text{g/L}$ on the upgradient side to $0.8 \mu\text{g/L}$ on the back side of the wall. It then rose to $1.3 \mu\text{g/L}$ on the downgradient side.
- Pb decreased along the plume's path from $4.4 \mu\text{g/L}$ at ML-2 to $3.0 \mu\text{g/L}$.
- Zn decreased from $3.53 \mu\text{g/L}$ at the upgradient well to $<20 \mu\text{g/L}$ at the front side of the wall and remained at that concentration along the path.

In general, sulfate reduction within the wall was indicated by decreases in SO_4^{2-} concentration, E_H levels and heavy metal concentrations and by increases in alkalinity, dissolved organic carbon and S^{2-} concentrations. Increases in heavy metal (Cu, Ni) concentrations downgradient of the wall were attributed to infiltration from sulfide ore impacted soils in the vadose zone and equilibration of treated water with contaminated soil solids.

References: McGregor *et al.*, 1999; USEPA, ITRC and RTDF, 1999.

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3.2.5 Summary of PRB Sites Treating Inorganic Compounds

The following sites have been previously described in the literature to a greater extent than those in the above sections. Therefore, only brief outlines are provided.

Nickel Rim, Sudbury, Ontario, Canada

Previous Site Operation: Mine
Installation Date: August 1995
Contaminants: Ni, Fe, SO₄²⁻
Reactive Materials: Municipal and leaf compost, wood chips mixed w/ pea gravel
Mechanism of Remediation: Biological (SRB) w/ metal sulfide precipitation
Wall Configuration: Continuous wall with sand buffer zones on up- and down-gradient sides
Wall Dimensions: 50' long x 14' deep x 12' thick
Installation Method: Cut and fill within a valley confined by bedrock
Results: Decreases in concentrations of all contaminants
pH from 5.8 to 7.0, alkalinity as CaCO₃ from 0 to 2000 mg/L.
Wall has potential to remain active for 15 years. Additional test cells have been installed
Sources of Information: Benner, Blowes and Ptacek, 1997; Blowes *et al.*, 1995; ITRC, 1998; RTDF, 1999a; USEPA, 1999, 1998
Contact: David Blowes, Waterloo Centre for Groundwater Research, University of Waterloo, Ontario, Canada
519-888-4878

Tonolli Superfund Site, Nesquehoning, PA

Previous Site Operation: Battery recycling and secondary lead smelting
Installation Date: August, 1998
Contaminants: Pb, Cd, As, Zn, Cu
Reactive Materials: Limestone
Mechanism of Remediation: pH control (resulting in decreases in metal solubility)
Wall Configuration: Continuous wall
Wall Dimensions: 1,100' long x 20' deep x 3' thick
Installation Method: Trackhoe
Results: No data yet, monitoring wells are not yet installed
Sources of Information: Banks, 1999; RTDF, 1999a; USEPA, 1999
Contact: John Banks, Remedial Project Manager, USEPA Region 3, Philadelphia, PA, 215-814-3214

U.S. Coast Guard Support Center, Elizabeth City, NC

Previous Site Operation: Electroplating shop
Installation Date: June, 1996
Contaminants: Cr(VI), TCE
Reactive Materials: ZVI
Mechanism of Remediation: Redox
Wall Configuration: Continuous wall
Wall Dimensions: 150' long x 24' deep x 2' thick; 450 tons granular Fe
Installation Method: Continuous trencher

Results: All Cr removed from 1st 6" of wall, none detected down-gradient, TCE and vinyl chloride below MCLs in all but 1 and 3 down-gradient wells, respectively

Pilot Scale Study: September 1994, 21 8"-diameter augered columns of 50% Fe/25% coarse sand/25% aquifer materials installed from 10-22' below ground surface in a 60 ft² area in a 3 hole array, Cr below detection, 75% TCE reduction, installation designed to optimize Cr removal, not chlorinated solvents.

Sources of Information: FRTR, 1999; GWRTAC, 1996; ITRC, 1998; RTDF, 1999a, 1998; USEPA, 1999, 1998, 1995; USEPA, Univ. of Waterloo, US Coast Guard, 1999

Contact: Bob Puls, USEPA National Risk Management Research Laboratory, Ada, OK, 580-436-8543

100 D Area, Hanford Site, Richland, WA

Previous Site Operation: Nuclear reactor, Cr containing anti-corrosion agents used

Installation Date: September 1997 (1 well in 1997, 4 others in 1998)

Contaminants: Cr(VI)

Reactive Materials: Sodium dithionite

Mechanism of Remediation: *In situ* redox manipulation

Wall Configuration: Continuous (overlapping injections)

Wall Dimensions: 150' long x 100' deep x 50' thick

Installation Method: Injection into 5 existing wells

Results: Cr(VI) < 8 µg/L after 1st well injected

Additional Information: Also analyzing reductant similar to kitty litter to reduce Cr(VI) to Cr(III), which is less mobile

Sources of Information: ITRC, 1998; RTDF, 1998, 1999a; USEPA, 1999, 1994

Contact: Jonathan Fruchter, Batelle Pacific Northwest National Laboratory, Richland, WA, 509-376-3937

Large Experimental Aquifer Program (LEAP) Demonstration Facility, Portland, OR

Previous Site Operation: None, contained simulated aquifer created and intentionally contaminated for research purposes

Installation Date: October, 1997

Contaminants: Cr(VI), PCE

Reactive Materials: Surfactant modified zeolites

Mechanism of Remediation: Sorption

Wall Configuration: Hanging barrier in perforated metal frame

Wall Dimensions: 20' long x 6.5' deep x 3' thick

Results: Retardation factors for both contaminants were on the order of 50

Sources of Information: Bowman *et al.*, 1999a,b; ESE, 1999; Roy, 1999; RTDF, 1999a; USEPA, 1999

Contact: Robert Bowman, Department of Earth and Environmental Science, New Mexico Tech, Socorro, NM, 505-835-5992

Public School, Langton, Ontario, Canada

Previous Site Operation: Septic system on school property
Installation Date: August, 1993
Contaminants: PO_4^{3-} , NO_3^-
Reactive Materials: Fe/Ca oxides, limestone, wood chips
Mechanism of Remediation: PO_4^{3-} : sorption on Fe oxides, precipitation w/ Ca
 NO_3^- : biological denitrification
Wall Configuration: Funnel and gate
Wall Dimensions: Funnels: 16' from gate, 5' below water table; gate: 6' long x 5' deep x 6' thick, 2' thick PO_4^{3-} treatment zone (6% Fe/Ca oxides, 9% limestone, 85% aquifer materials) 4' thick NO_3^- treatment zone (wood chips)
Installation Method: Conventional
Results: Decreases in both contaminants were noted on the down-gradient sides (PO_4^{3-} : <2 mg/L, NO_3^- : 0.3 mg/L)
Sources of Information: RTDF, 1999a; USEPA, 1999, 1998
Contact: David Blowes (PO_4^{3-})--519-888-4878
Will Robertson (NO_3^-)--519-888-4567 ext. 6800
Dept. of Earth Sciences, University of Waterloo, Ontario

Savannah River TNX Area, Aiken, SC

Current Site Operation: Semi-works facility for the Savannah River Technology Center
Installation Date: July 1997
Contaminants: Chlorinated solvents, NO_3^-
Reactive Materials: ZVI
Mechanism of Remediation: Redox
Wall Configuration: GeoSiphon cell
Results: Phase I: completed 12/97, induced by pumping TCE degradation is rate limiting
Phase II: used siphon to get 2.7 gal/min flow
Phase III: will involve full scale system to capture entire plume
Sources of Information: RTDF, 1998; USEPA, 1999
Contact: Mark Phifer, Westinghouse SRC/SRS, Aiken, SC
803-725-5222

Fry Canyon Site, UT

Previous Site Operation: Uranium upgrader
Installation Date: August 1997
Contaminants: U

Reactive Materials: ZVI, amorphous ferric oxide, bone char PO_4^{3-}
 Mechanism of Remediation: Redox, sorption
 Wall Configuration: Funnel and gate
 Wall Dimensions: 3 gates (1 for each medium), impermeable gravel in between each gate, 18' long bentonite wall on left side, 7' long x 4' deep x 3' thick, 110 ft^3 of material in each gate
 Installation Method: Conventional
 Results: 99.9% input U removed from ZVI, less removal from other 2, except for 2 monitoring periods > 90% U removed by PO_4^{3-} Fe oxide removed > 90% U through 11/97, < 90% U removed from 1/98-9/98
 Sources of Information: DOEGJO, 1999; Feltcorn and Breeden, 1997; ITRC, 1998; RTDF, 1999a; USEPA, 1999; USGS, 1999
 Contact: Ed Feltcorn, USEPA/ORIA, Washington, DC, 202-564-9422
 David Naftz, USGS, Salt Lake City, UT, 801-975-3389

Uranium Mill Tailings Remedial Action (UMTRA) Site, Durango, Co

Previous/current Site Operation: Uranium mill tailings disposal site
 Installation Date: Four reactors constructed October 1995:
 "C" operated May 1996-March 1998
 "B" started April 1998
 "A" and "D" testing scheduled for 1999
 Contaminants: U, Mo, NO_3^- (As, Mn, NH_3 , Se, V analyzed to a lesser extent)
 Reactive Materials: "C": ZVI (foamed Fe), "A" and "D": steel wool
 "B": steel wool and copper wool
 Mechanism of Remediation: Redox (possible biological denitrification from high hydrogen environment produced by iron)
 Wall Configuration: "C" and "D": 2 baffle style boxes/tanks
 "A" and "B": 2 horizontal beds/leach field
 All four connected by distribution box
 Wall Dimensions: Boxes: 1.8 x 1 x 1.2 m, beds: 4.5 x 9 x 0.3 m
 Results: "C": obstructed and closed in March 1998, H_2 / CH_4 gas found
 "B": reduced concentrations of all of above contaminants
 Sources of Information: DOEGJO, 1999; GWRTAC, 1996; RTDF, 1998;
 Contact: Brian P. Dwyer, 505-845-9894
 George C. Allen, 505-844-9769
 Sandia National Laboratory, Albuquerque, NM

Permeable Reactive Treatment (PeRT) Wall, Monticello, UT

Previous Site Operation: Uranium and vanadium processing mill
 Installation Date: June 30, 1999
 Contaminants: As, Mn, Mo, Se, V, U, Pb
 Reactive Materials: ZVI

Mechanism of Remediation: Redox
 Wall Configuration: Funnel and gate
 Wall Dimensions: Funnel: 300' soil-bentonite slurry wall keyed into bedrock 12-24' below surface
 Gate: 100' long x 17' deep x 10' thick surrounded by pre- and post-treatment gravel packs
 Installation Method: Conventional with temporary sheet piling
 Results: Recently installed
 Sources of Information: Cromwell, 1999; ITRC, 1998; RTDF, 1998
 Contact: Vernon Cromwell, DOE Grand Junction Office, Grand Junction, CO, 970-248-7735

DOE Rocky Flats Environmental Technology Site, Golden, Co

Previous Site Operation: Drum and coolant disposal at Mound Site Plume
 Installation Date: Mid-1998
 Contaminants: Chlorinated solvents, americium, uranium
 Reactive Materials: Iron filings
 Mechanism of Remediation: Redox, sorption
 Wall Configuration: Groundwater collection system at trench bottom to cells impermeable geomembrane on down-gradient side trench backfilled with filter pack
 Trench Dimensions: 230' long x 15-20' deep x 2-3' thick
 Installation Method: Conventional, keyed into claystone
 Results: None given, plans to a build 1300' long collection system coupled with centralized reactive metals treatment system and a PRB system for NO₃⁻ /U plume from solar evaporation ponds
 Sources of Information: ITRC, 1998; RTDF, 1998
 Contact: Annette Primrose, Rocky Mountain Remediation Services, Golden, CO, 303-966-4385

Appendix A: PRBs on the Web

Government

Federal Remediation Technologies Roundtable <http://www.frtr.gov>

US Geological Survey

Fry Canyon Home Page <http://svr1dutslc.wr.usgs.gov/fry/fry.html>

Department of Defense

Environmental Security Technology Certification Program <http://www.estcp.org/>

Environmental Protection Agency

Home Page <http://www.epa.gov>

Technology Innovation Office <http://clu-in.org>

<http://www.epa.gov/tio>

Robert Kerr Research Laboratory <http://www.epa.gov/ada/kerrcenter.html>

Ground Water Currents <http://clu-in.org/products/newsltrs/gwc/>

Department of Energy

Environmental Management Technical Information Exchange <http://www.em.doe.gov/tie>

Definitions of walls www.em.doe.gov/define/techs/remdes2.html#313

Subsurface Contaminants Focus Area <http://www.envnet.org/scfa/>

Grand Junction Office <http://www.doegjpo.com/projects/propage1.htm>

Sandia National Laboratory <http://www.sandia.gov/Subsurface/projects2.html#remediation>

Academia

New Mexico Tech, Dr. Bowman, SMZ <http://zippy.nmt.edu/Hydro/faculty/Bowman/>

Oregon Graduate Institute of Science and Technology <http://cgr.ese.ogi.edu>

University of Waterloo <http://www.crestech.ca/research/water/remediation/remediation.htm>

University of Rice <http://www.ruf.rice.edu/~aatdf/pages/passive.htm>

Industry/Consulting

EMCON (search for “sand-fracking”) <http://www.emconinc.com>

EnviroMetal Technology <http://www.beak.com/technologies/eti.htm>

General Electric Research and Development <http://www.crd.ge.com/cptl/cntwater.htm>

Geo-Con, Inc. <http://www.geocon.net/page3.htm>

Powell and Associates <http://www.powellassociates.com/sciserv/SciServmain.html>

Stearns and Wheler <http://www.stearnswheler.com/main.htm>

Partnerships

Center for Public Env Oversight <http://www.cpeo.org/techtree/ttdescript/permbarr.htm>

Ground Water Remediation Technologies Analysis Center <http://www.gwrtac.org/html/techs.html>

Remediation Technologies Development Forum <http://www.rtdf.org>

USEPA, USCG, U. of Waterloo: Elizabeth City site <http://www.epa.gov/ahaazvuc/eliz.html>

Appendix B: Design Calculations

First order degradation kinetics:

$$C_t = C_0 e^{-\lambda t}$$

$$t_{1/2} = \ln 2 / \lambda.$$

$$\lambda = -[\ln (C/C_0)] / t$$

$$\lambda = \ln 2 / t_{1/2}$$

$$t = [\ln (C/C_0)] / -\lambda$$

Sizing thickness (T):

$$T = t_{res} \times V$$

$$V = ki/n$$

$$n = [1 - \text{bulk density} / \text{particle density}]$$

$$n' = 100\% [1 - \text{bulk density} / \text{particle density}]$$

Materials Costs:

$$\$\$ = (\text{plume X area}) \times (\$/\text{weight}) \times (\text{weight} / \text{X area})$$

$$\$\$ = \text{cubic volume} \times 0.08 \text{ tons/cubic foot} \times \$425/\text{ton}$$

Installation Costs:

$$\$\$ = (\text{plume X area}) \times (\$/\text{volume}) \times (\text{mass} / \text{X area}) \times (\text{mass}/\text{volume})$$

C=concentration (mass/volume)
t=time (time)
 $t_{1/2}$ = half life (time)
 λ =rate constant (time⁻¹)
T=thickness (distance)
V=velocity (distance/time)
k=hydraulic conductivity (distance/time)
i=hydraulic gradient (unitless)
n=porosity (unitless)
n'=percent porosity (unitless)
x area=cross sectional area (distance²)

Appendix C: PRBs at a Glance

Contaminants	Metals, nutrients, radionuclides
Media	ZV metals, organic carbon, sodium dithionite, limestone, SMZ, phosphate, bone char, hydrated lime, polysulfide compound
Installation Techniques	Trench and fill, continuous trenching, tremie tube, hydrofracturing, jetting, deep soil mixing
Site Characterization Concerns	Plume characteristics, hydrogeology, geochemistry, microbiology
Mechanisms	Redox, sorption, solid precipitation (can be biological)
Advantages	<i>In situ</i> , low costs, not energy intensive, passive, site can be returned to economic use
Concerns	Must catch entire plume, precipitate clogging, corrosion of media, toxic byproducts, remediation can be slow
Basic Wall Designs	Continuous trench, funnel and gate

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